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SUPPORTING INFORMATION

<u>**DOI**</u>: 10.1002/ejic.201402587 <u>**Title**</u>: Synthesis of Atomically Precise Silver Clusters by Using the Miscibility Principle <u>**Author(s)**</u>: Atanu Ghosh, Thalappil Pradeep*

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S1. Supporting information

Phase transfer agent: Phase transfer agent (PTR) is a catalyst which transfers reactant from one phase to another phase where a process occurs. Tetraoctylammoniumbromide (TOABR), one such PTR, has been widely used in gold nanoparticle synthesis which transfers gold ions from the aqueous to the organic phase, to carry out reactions in the organic medium. To transfer 30 mL 30 mM HAuCl₄ from water to toluene phase, 80 mL 50 mM TOABR is needed (M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, *J. Chem. Soc., Chem. Commun.*801, 1994). It has been well-established that PTR is a persistent impurity in monolayer protected nanoparticles and it affects the properties of the monolayers (Mukhopadhyay, R.; Mitra, S.; Johnson, M.; Rajeev Kumar, V. R.; Pradeep, T. *Phys. Rev. B* 2007, 75, 075414; Kumar, V. R. R.; Mukhopadhyay, R.; Pradeep, T. *J. Chem. Sci. (Bangalore, India)* 2008, *120*, 537).

Experimental section: Compositions used in Figure 1: First we dissolved 20 mg of silver nitrtate in a fixed quanity of methanol (see below for the volumes used for various points in the figure). To that, a fixed quanity of toluene and 132 μ L BBSH (4-tert-Butylbenzyl mercaptan) were added under stirring. The color of the solution changes colorless to yellowish white. After 30 min, we added a definite volume of ice cold water containing 45 mg of NaBH₄ under stirring. We continued stirring for 90-120 min. This ended up with two phases, toluene rich and water rich phases. Then small amount of the sample from the toluene rich phase was taken out and MALDI MS was taken using DCTB (trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile) as the matrix. UV-vis spectrum of the sample was measured using toluene as the solvent. In case of points a, b, c and d, we have done the reaction at the same condition and reactant compositions but varied the solvent compositions. Below we have shown the solvent percentages (mole fraction) used at respective points in Figure 1.

Point	Methanol	Water	Toluene
а	20%	65%	15%
	1.82 mL	2.63 mL	3.55 mL
b	65%	15%	20%
	4.19 mL	0.45 mL	3.36 mL
С	15%	20%	65%
	0.63 mL	0.37 mL	6.97 mL
d	35%	52%	13%
	3.00 mL	2.00 mL	3.00 mL

Analytical methods:

UV-vis measurement: Perkin Elmer Lambda 25 UV-vis spectrometer was used for the measurements. Spectra were measured typically in the range of 190-1100 nm.

TEM measurement: TEM images were collected using a JEOL 3010 microscope. A diluted solution of Ag₆₈ was spotted on a carbon coated copper grid and was dried in laboratory ambience. Images were collected at 200 keV to reduce beam-induced damage.

Fourier-transform infrared (FT-IR): FT-IR spectrum of Ag₆₈ was measured with a Perkin Elmer Spectrum One instrument. For sample preparation, KBr crystals were used as the matrix.

SEM and EDAX analyses: Scanning electron microscopic (SEM) and energy dispersive X-ray (EDAX) analyses were done in a FEI QUANTA- 200 SEM. For measurements, samples were drop-casted on an indium tin oxide coated conducting glass and dried in vacuum. It was died in air and used for analysis.

HPLC: HPLC experiments were conducted on a Shimadzu instrument consisting of a CBM-20A controller, DGU-20AR on-line degasser, LC-20AD pump, SIL-20A auto-sampler, CTO-20A column oven, and SPD-M20A photodiode array (PDA) detector. A stainless steel column (250x4.6 mm inner diameter) packed with 5-µm C18 bonded silica with 300-Å pore size (Theromo Scientific) was used as the reverse-phase column. The column temperature was maintained at 25 °C. The absorbance chromatogram was monitored by a PDA detector at 320 nm. The absorption spectra of the eluted peaks were collected over 190–800 nm by the PDA detector.

MALDI and LDI MS: The mass spectrometric studies were conducted using a Voyager DE PRO Bio spectrometry Workstation (Applied Biosystems) MALDI TOF MS instrument. A pulsed nitrogen laser of 337 nm was used for desorption ionization and TOF was operated in the delayed extraction mode. Typical delay times employed were of the order of 75–150 ns. The mass spectra were collected in the positive mode and were averaged for 200 shots. Most of the measurements were done in the reflectron mode. To study the time dependent MALDI MS of Ag₆₈, each time 1.5 μ L of the sample was taken from the reaction bottle and mixed with 2.5 μ L of DCTB matrix which was prepared in toluene. Then the mixture was spotted on the target plate. The plate was left to dry in air and inserted into the spectrometer. It was assumed that after spotting, there was no progress of the reaction. It is important to point out that MALDI MS was measured at threshold laser powers which result in spectra at no or reduced fragmentation (A. Dass, *J. Am. Chem. Soc.* 2008, *130*, 5940). In case of LDI MS, only 2.5 μ L of the sample was spotted on the plate and dried in air. Then the plate was inserted into the spectrometer.

S2. Supporting information

MALDI MS and UV-vis spectra of the samples prepared at different solvent compositions



Figure S2. MALDI MS of the samples prepared at different regions of the phase diagram, keeping the same reactant composition. It confirms the formation of different cluster cores. Inset: UV-vis spectra of the samples, in toluene solvent.

S3. Supporting information Blank experiments with solvents



Figure S3. Photographs represent miscibility experiment of solvents. (A) Only 3 ml methanol, (B) mixture of 3 ml methanol and 3 ml toluene, appearing as a single phase and (C) when 2 ml water is added to (B), water-methanol form a phase which is separated from toluene rich phase. (D) If toluene is replaced with chloroform, chloroform rich phase will come down and the methanol rich phase goes up. Phase boundaries are marked.

S4. Supporting information EDAX spectra of two separated phases

Upon centrifugation, insouble thiolates precipitate in methanol/water part. By this way we have discarded the excess thiolate. Below Figure 1a and 1b are the EDAX spectra of methanol/water and toluene phases, respectively. To prepare the samples for EDAX, first we have separated the two phases. Then we had drop cast the samples on two different conducting glass plates and dried under vacuum. Figures 1a and 1b (below) are the EDAX spectra of methanol/water and toluene phases, respectively. Figure 1a shows that silver and sodium ions are present in methanol/water and sulphur is absent. This means that thiol/thiolate is absent in this phase. Figure 1b shows that higher amount of sulphur i.e thiol is present in toluene phase and sodium ions are almost absent in it.



Figure S4. EDAX spectra of (a) methanol/water and (b) toluene phases, respectively.

S5. Supporting information Reaction in methanol

Silver nitrate is soluble in methanol but insoluble in toluene. We have performed the same reaction only in methanol. The following figures show the importance of mixed solvents in comparison to methanol alone.



Figure S5. (A-C) Photographs for the synthesis done in methanol alone. (A) Ag(I)SBB thiolate in methanol alone. B) After addition of 45 mg 2 mL aq NaBH₄ to Ag(I)SBB thiolate. C) The precipitate in B was dispersed in toluene. D) Synthesis done in methanol-toluene mixture.

S6. Supporting information Large scale synthesis

In a larger scale synthesis, 160 mg of silver nitrate was dissolved in 24 ml of methanol. To that 24 ml of toluene was added. 800 μ L of BBSH thiol was added to it under stirring condition. The color of the solution changes to light yellow and then yellowish white. It confirms the formation of Ag(I)SBB thiolate. The solution contained single phase at this stage. After 30 minutes, 16 ml of ice cold solution containing 360 mg of NaBH₄ was added to it under stirring condition. The color changes from light brown to dark brown. Time dependent UV-vis spectra were taken. The reaction took 120 minutes to complete. After 10 minutes of waiting, cluster containing toluene rich phase was separated from the methanol rich phase. It was rotavapored and the product was washed with methanol 3-4 times to get the dark brown powder of Ag₆₈SBB₃₄.



Figure S6. A photograph of the large scale synthesis. Top brown colored toluene rich layer contains the cluster. Bottom methanol rich layer contains the reduction byproducts and other unreacted materials.

S7. Supporting information TEM, effect of electron beam irradiation



Figure S7. (A) TEM image of Ag₆₈SBB₁₄. (B-D) The cluster upon the irradation with the electron beam. TEM images were taken from the same area after 5, 10 and 15 minutes of irradiation in B, C and D, respectively. Size of the cluster increases due to electron beam irradation. Insets of figure (A) and (D) represent the histrograms of size distribution.

S8. Supporting information MALDI and LDI MS



Figure 8. i) Schematic illustration of the effect of direct laser irradiation on ligand on the cluster. ii) Comparison of MALDI and LDI MS.

S9. Supporting information TGA



Figure S9. Thermogravimetric analysis under nitrogen atmosphere shows a weight loss of 44.8% which supports the expected value (45%) due to the organic fraction present in the cluster.

S10. Supporting information SEM/EDAX



Figure S10. (A) EDAX spectrum of Ag₆₈SBB₃₄ and (B) SEM image of Ag₆₈SBB₃₄ aggregate from which the EDAX spectrum was taken. Ag:S atomic ratio measured is 1:0.51, as expected (actual is 1:0.50).

S11. Supporting information SEM image of the crystallites



Figure S11. SEM image of the sample after crystallization.

S12. Supporting information

FT-IR



Figure S12. Expanded FT-IR of BBSH and Ag₆₈SBB₃₄; the disappearance of the peak at 2562 cm⁻¹ (in the spectrum of Ag₆₈SBB₃₄) indicated that the S-H bond was absent in it. This proved that sulphur is connected to the metal ion in the thiolate form. Inset: An expanded cluster spectrum.

S13. Supporting information XRD



Figure S13. Comparison of the X-ray diffraction patterns (XRD) of the Ag₆₈SBB₃₄ cluster (red) and Ag@H₂MSA (15 nm) nanoparticle (green).The diffraction peaks are marked.

S14. Supporting information

XPS



Figure S14. (A) XPS survey spectrum of the as synthesized Ag₆₈(SBB)₃₄. (B), (C) and (D) represent the XPS spectra for Ag 3d, S 2p and C 1s, respectively with multiple component fitting. It shows that Ag is almost in the zero oxidation state.

S15. Supporting information

Time dependent UV-vis spectra



Figure 15. Time dependent UV-vis spectra for the cluster during synthesis.

S16. Supporting information Different clusters prepared



Figure S16. (A-D) Mass spectra for the four different clusters prepared by this method. Insets show the UV-vis spectra for the corresponding cluster. Here L is 4-tert-butylbenzenethiol. The conditions are listed below.

20 mg AgNO₃	1: 4 thiol (88 μL)	1: 6 thiol (132 μL)
1:5 NaBH ₄ (22.5 mg)	8.0 kDa	-
1:7 NaBH ₄ (37 mg)	22.8 kDa	-
1:10 NaBH ₄ (45 mg)	29.2 kDa	34.4 kDa

S17. Supporting information



Figure S17. UV-vis spectrum of Au₂₅(SBB)₁₈ prepared by the reported method. The spectrum matches with that of a standard sample. Inset: MALDI MS spectrum of Au₂₅(SBB)₁₈ in the negative mode. Fragmented product is marked with an asterisk (*). It is due to Au₂₁(SBB)₁₄.