Supporting Materials

From Understanding the Roles of Tetraoctylammonium Bromide in the Two-Phase

Brust-Schiffrin Method to Tuning the Size of Gold Nanoclusters

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Experimental section: Materials and Instrumentation.

Ultrapure Millipore water (18.2 M Ω) was used in the experiments. All glassware and stirring bars were washed with aqua regia (HCl/HNO₃ volume ratio = 3:1), rinsed with alcohol and water, and dried in an oven before use. Benzeneselenol (PhSeH), hydrogen tetrachloroaurate (III) hydrate (HAuCl₄·3H₂O), cyclohexanethiol (HS-*c*-C₆H₁₁) and tetraoctylammonium bromide (TOAB) from Sigma-Aldrich, sodium borohydride (NaBH₄) from Merck, deuterated toluene and D₂O from Cambridge Isotope Laboratories, toluene and ethanol from Fisher, and sodium hydroxide (NaOH) from Kanto Chemical were used as received.

UV-vis absorption spectra were recorded on an Agilent 8453 spectrometer. ESI-MS was conducted on an Agilent 6210 time-of-flight LC/MS system. Samples of 5 µL were directly injected into the chamber. The following parameters were used: flow rate of the eluent (acetonitrile), 0.3 mL·min⁻¹; capillary voltage, 4 kV; nebulizer, 48 psig; dry gas, 4.5–7 L·min⁻¹ at 350 °C; m/z range, 100–10000. 1H NMR analysis was performed on a Bruker AV-400 (400 MHz) spectrometer at 25 °C. The binding energies of Au species in Au NCs were determined by XPS on a Kratos AXIS UltraDLD spectrometer. The yields of Au NCs were assessed by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7700 ICP-MS system. In order to precisely analyze the yields of the Au NCs, the Au NC solutions was treated to separate the Au NC samples from PhSe-Au(I) complexes, since a small amount of PhSe-Au(I) complexes (unreacted or from NC decomposition) might be present in the solution of Au NCs. The detailed treatment procedure is as follows. After synthesizing selenolated Au NC species, the aqueous phase of the sample was removed, while the organic phase was evaporated and then washed several times with CH₃OH/hexane to remove excess selenolate. Next, the Au NCs were separated from PhSe-Au(I) complexes by extraction with DCM or toluene (note: PhSe-Au(I) complexes was poorly soluble in almost all solvents).^[1]Lastly, the Au NC solutions were

dried again and treated with diluted HNO₃ to attain Au ions for subsequent ICP-MS analysis. The dynamic diameters of TOAB micelles and PhSe-Au(I) complexes were measured by DLS with a Malvern (ZEN 3600) Zetasizer Nano ZS. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F20 electron microscope operating at 200 kV.

Synthesis of Selenolate-Protected Au NCs.

Aqueous solution of HAuCl₄ (50 mM) was prepared with ultrapure water, while hydrophobic PhSeH ligands (50 mM) and TOAB (50 mM) were dissolved in toluene. Aqueous solution of NaBH₄ was prepared by dissolving 43 mg of NaBH₄ powder in 10 mL of 0.2 M NaOH solution. In a typical synthesis of selenolated Au NCs, toluene solution of PhSeH (50 mM, 0.175 mL) and aqueous solution of HAuCl₄ (50 mM, 0.1 mL) were first mixed in toluene (4.8 mL) and water (4.5 mL), and stirred for 1 h to facilitate the formation of selenolate-Au(I) complexes in toluene, followed by adding a certain volume of TOAB (1 μ L for Au₁₈(PhSe)₁₄; 10 μ L for Au₂₅(PhSe)₁₈; 20 μ L for Au₂₃(PhSe)₁₆; 40 μ L for Au₃₁(PhSe)₂₀), aqueous NaOH solution (1 M, 0.4 mL), and aqueous NaBH₄ solution (0.1 mL) under stirring condition. After an additional 3 h of reaction, the selenolated Au NCs in organic phase were directly collected for UV-vis absorption analysis without any post-treatment.

Prior to ESI-MS characterization, an additional purification was conducted to remove interference species such as TOAB and unreduced PhSe-Au(I) complexes from NC solution. Typically, after removing the aqueous phase, the mixture in the organic phase was dried via rotary evaporation at 40 °C. Afterwards, the samples were washed with CH₃OH/hexane, re-dissolved with toluene, and centrifuged (after introducing abundant CH₃OH); this was repeated several times to remove excess TOAB. Subsequently, the selenolate-protected Au NCs were further separated from PhSe-Au(I) complexes by extraction with dichloromethane (note: PhSe-Au(I) complexes are poorly soluble in almost all solvents). The Au NCs obtained were dissolved in toluene for ESI-MS analysis.

Synthesis of Thiolate-Protected Au NCs.

In a typical synthesis of thiolated Au NCs, toluene solution of cyclohexanethiol (50 mM, 0.2 mL) and aqueous solution of HAuCl₄ (50 mM, 0.1 mL) were first mixed in toluene (4.8 mL) and water (4.5 mL) and stirred for 5 min to facilitate the formation of thiolate-Au(I) complexes in toluene, followed by adding toluene solution of TOAB (50 mM, 5 μ L), aqueous NaOH solution (1 M, 0.4 mL) and aqueous NaBH₄ solution (0.1 mL) under stirring condition. After another 3 h of reaction, the thiolated Au NCs in organic phase were directly collected for UV-vis absorption analysis without any post-treatment.

Prior to ESI-MS characterization, an additional purification was conducted to remove interference species such as TOAB and unreduced thiolate-Au(I) complexes from the NC solution. Typically, after removing the aqueous phase, the mixture in the organic phase was dried via rotary evaporation at 40 °C. Afterwards, the samples were washed with CH₃OH, redissolved with toluene, and centrifuged (after introducing abundant CH₃OH); this was repeated several times to remove excess TOAB. Subsequently, thiolated Au NCs were further separated from thiolate-Au(I) complexes by extraction with dichloromethane. The Au NCs obtained were dissolved in toluene for ESI-MS analysis.

Supplementary figures:



Figure S1. ¹H NMR spectra of the organic layer of (a) TOAB (0.06 mmole or 60 mM) in 1 mL of deuterated toluene mixed with 1 mL of D_2O , and (b) TOA-Au(III)X₄ complexes prepared by mixing TOAB (0.06 mmole, 1 mL) in deuterated toluene with HAuCl₄ solution (0.02 mmole or 20 mM, 1 mL) in D_2O and stirring for 1 h.



Figure S2. Isotope patterns acquired theoretically (red curve) and experimentally (black curve) for TOAB species identified in the upper panel of Figure 1b.



Figure S3. Isotope patterns acquired theoretically (red curve) and experimentally (black curve) for TOA-Au(III)X₄ complexes identified in the lower panel of Figure 1b.



Figure S4. Isotope patterns acquired theoretically (red curve) and experimentally (black curve) for TOA-BH₄ complexes identified in Figure 1d.



Figure S5. (a) UV-vis absorption spectrum and (b) a representative TEM image of the TOABstabilized Au NPs. The TOAB-stabilized Au NPs are synthesized by mixing aqueous solution of HAuCl₄ (50 mM, 0.2 mL) with toluene solution of TOAB (10 mM, 5 mL) in water (4.5 mL) under stirring condition, followed by adding aqueous NaOH solution (1 M, 0.02 mL), and aqueous NaBH₄ solution (0.2 mL) under stirring condition for 30 mins.



Figure S6. Enlarged ¹H NMR spectra of the organic layer of (a) TOAB (0.06 mmole or 60 mM) in 1 mL of deuterated toluene mixed with 1 mL of D_2O , (b) TOA-Au(III)X₄ complexes prepared by mixing TOAB (0.06 mmole, 1 mL) in deuterated toluene with HAuCl₄ solution (0.02 mmole or 20 mM, 1 mL) in D_2O and stirring for 1 h, (c) TOA-Au(I)X₂ complexes derived from reducing TOA-Au(III)X₄ complexes (the same as that used in Figure S6b) by PhSeH (0.06 mmole) and stirring for 1 h, and (d) TOA-BH₄ complexes prepared by mixing TOAB (0.06 mmole, 1 mL) in D_2O and stirring for 1 h, and (d) TOA-BH₄ complexes prepared by mixing TOAB (0.06 mmole, 1 mL) in D_2O and stirring for 10 min.



Figure S7. (a) ¹H NMR spectra and (b) the enlarged ¹H NMR spectra of the organic layer acquired by mixing TOAB (0.06 mmole or 60 mM, 1 mL) in deuterated toluene with HAuCl₄ solution (0.02 mmole or 20 mM, 1 mL) in (i) 1 mL of D_2O (black curves), (ii) 0.75 mL of D_2O and 0.25 mL of H₂O (blue curves), and (iii) 0.5 mL of D_2O and 0.5 mL of H₂O (red curves).

The proportional increase in intensity of the peak at ~5.4 ppm (Figure S7b) revealed that this peak corresponded to encapsulated water within the TOAB micelles.



Figure S8. DLS of the toluene layer of TOAB (0.06 mmole or 60 mM, 1 mL, black curve) in toluene with 1 mL of H₂O. TOA-Au(III)X₄ complexes (red curve) were prepared by mixing TOAB (0.06 mmole, 1 mL) in toluene with aqueous HAuCl₄ solution (0.02 mmole or 20 mM, 1 mL) in H₂O and stirring for 1 h. TOA-BH₄ complexes (blue curve) were prepared by mixing TOAB (0.06 mmole or 60 mM, 1 mL) in toluene with NaBH₄ solution (~7.566 mg or 0.2 mmole, 1 mL) in H₂O and stirring for 10 min. DLS diameters of these three samples were ~2000 nm, suggesting the formation of TOAB micelles.



Figure S9. Isotope patterns acquired theoretically (red curve) and experimentally (black curve) for PhSeH and PhSe-Au(I) complexes shown in Figure 2b.



Figure S10. Effect of the TOAB on the reduction of PhSe-Au(I) complexes in a two-phase system. (a) UV-vis absorption spectra and (b) ESI mass spectra of the PhSe-Au(I) complexes before (black curves) and after (blue curves) adding reducing agent NaBH₄ without the usage of TOAB, while keeping all other synthetic conditions unchanged. The inset shows photograph of the solution of PhSe-Au(I) complexes before (left item) and after (right item) adding the reducing agent NaBH₄. No changes in the UV-vis absorption spectra and the ESI mass spectra were observed before and after adding NaBH₄, indicating that reduction could not occur without the participation of TOAB in the reaction system.



Figure S11. Isotope patterns acquired theoretically (red curve) and experimentally (black curve) for TOA-BH₄ species shown in Figure 2d.



Figure S12. UV-vis absorption spectra and photographs (inset) of the PhSe-Au(I) complexes before (black curve) and after (blue curve) adding the toluene solution of TOA-BH₄ complexes. The toluene solution of TOA-BH₄ complexes was prepared by mixing TOAB (0.5 mM, 1 mL) in toluene with NaBH₄ solution (~112 mM, 1 mL) in H₂O and stirring for 10 min. Five minutes after adding the toluene solution of TOA-BH₄ complexes into the toluene solution of PhSe-Au(I) complexes, the solution color changed from light yellow to dark brown, indicating the formation of Au NCs.



Figure S13. DLS spectrum of the toluene layer of TOA-BH₄ species prepared by mixing TOAB (0.5 mM, 1 mL) in toluene with NaBH₄ solution (\sim 112 mM, 1 mL) in H₂O, and stirring for 10 min.



Figure S14. Representative TEM images of (a) $Au_{18}(PhSe)_{14}$, (b) $Au_{25}(PhSe)_{18}$, (c) $Au_{23}(PhSe)_{16}$, and (d) $Au_{31}(PhSe)_{20}$ NCs.



Figure S15. Isotope patterns acquired theoretically (red curve) and experimentally (black curve) for the as-synthesized Au NC species shown in Figure 3b.



Figure S16. Au(4f) XPS spectra of as-synthesized selenolated Au NCs. The vertical dotted lines represent the Au(4 $f_{7/2}$) binding energies of PhSe-Au(I) complexes and Au(0) film. The PhSe-Au(I) complexes were prepared as a reference by mixing HAuCl₄ with PhSeH in toluene/ethanol solution (molar ratio = 1:1).



Figure S17. (a) UV-vis absorption spectrum and photograph (inset), and (b) ESI mass spectrum of as-synthesized thiolated $Au_{23}(S-c-C_6H_{11})_{16}$ NCs.

Reference

[1] S. M. Reilly, T. Krick, A. Dass, J. Phys. Chem. C 2010, 114, 741.