

Supporting Information

Mechanistic insights on one-phase vs. two-phase Brust-Schiffrin method synthesis of Au nanoparticles with dioctyl-diselenides

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Chemicals:

Selenium (100mesh, 99.5%), sodium borohydride (powder, 98%), 1-bromohexane (98%), 1-bromooctane (99%), 1-bromododecane (97%), tetrahydrofuran (>99.0%), dichloromethane (99.8%), methanol (>99.9%), and hexanes (>98.5%) were purchased from Aldrich. Acetonitrile and toluene were bought from Fisher Chemicals, while ethanol was from Graham Company, hydrogen tetrachloroaurate hydrate (49 wt% Au) from Stem Chemicals, and tetra-*n*-octylammonium bromide (TOAB, 98%) from Alfa Aesar. All chemicals were used as received and all the glassware was cleaned in sulfuric acid with Nochromix and washed with Milli-Q water in all the experiments (18.2 MΩ·cm).

Instrumentation:

NMR. ¹H and ¹³C spectra were obtained using a Bruker AM 300 MHz spectrometer that was coupled with a Tecmag DSPECT acquisition system. The ¹H (7.16 ppm) and ¹³C (128.39 ppm) peaks of C₆D₆ were used as reference. OriginPro8 program was used for peak integration.

TEM. The TEM characterization was performed on JEOL JEM-2100 LaB₆ transmission electron microscope at 100 kV. The samples were prepared by dissolving NPs in toluene. Depending on the concentration, one to three drops were applied on the carbon-coated copper grids (200 mesh, Electron Microscopy Science), and then air dried, while the sizes of NPs were measured by ImageJ program.

Raman spectroscopy. The spectra were obtained using a confocal microprobe Raman system (Renishaw RM1000) equipped with a deep depletion CCD peltier cooled down to -70°C. The microscope attachment was based on an Olympus BH2-UMA system and a 50x-long working-length objective (8 mm) was used. A holographic notch filter was used to filter the exciting line and two selective holographic gratings (1200 g/mm and 2400 g/mm) were employed with respect to the required spectral resolution. The exciting wavelength was 785 nm from diode laser with a max power of 27 mW and a spot of ca. 3 μm on the surface. The spectroscopy was calibrated with the peak at 520 cm⁻¹ of clean Si wafer. Liquid sample was measured in 5-mm NMR tube. Solid or slurry sample was measured on clean microscope slide.

X-Ray Photoelectron Spectroscopy (XPS). XPS spectral data were acquired on a Kratos Axis Ultra DLD using an Al Kα (1486.7 eV) source. Samples were drop-casted from sonicated toluene suspensions onto cleaned Si substrates. Experiments were run three times on different spots of the same sample and the results were averaged.

Theoretical Calculations. Calculations were carried out for HAuCl₄, AuCl₄⁻, X₂Au–Se(C₈H₁₇)(OH)X (X=Cl, Br), XYAu–Se(C₈H₁₇)XY (X,Y=Cl, Br), and (C₈H₁₇Se)₂ at the B3LYP/cc-pVDZ level of theory (the cc-pVDZ-PP pseudopotential basis set was used on Au) using the GAMESS quantum chemistry program. All structures were fully optimized at the

stated level of theory. Vibrational frequencies were computed using two-sided numerical differencing of the analytic gradient.

Synthesis and Preparations:

Synthesis of (C8Se)₂. Dialkyl diselenides were synthesized from our previously reported work¹ with the additional purification step, where the silica/hexanes column (60 cm in length and 6 cm in diameter) was used.

Synthesis of Intermediates. For one-phase BSM, the mixture of (HAuCl₄, 0.05 mmol) aqueous solution (0.35 ml, 0.1329M) was mixed with (C₈H₁₇Se)₂ (0.025 mmol) in THF (5.0ml). (After the addition of (C8Se)₂ no color change was noted, the solution stayed yellow even after stirring overnight.) This mixture of HAuCl₄ and (C8Se)₂ with the ratio of 1Au : 0.5(C8Se)₂ was stirred in THF overnight, then rotary-evaporated, and C₆D₆ (0.8 ml) was added to run NMR experiments. The same concentrated intermediate solution was used for Raman (a couple of drops) and XPS measurements, where the experiments were run after C₆D₆ evaporated leaving solid for characterization behind. For two-phase BSM, the mixture of hydrogen tetrachloroaurate (HAuCl₄, 0.05 mmol) aqueous solution (0.35 ml) was mixed with a TOAB (0.15 mmol for ratio of 3TOAB : 1Au, 0.10 mmol for ratio of 2TOAB : 1Au, and 0.05 mmol for ratio of 1TOAB : 1Au, respectively) in 0.8 ml of C₆D₆. The solution turned burgundy red in color. Then (C₈H₁₇Se)₂ (0.025mmol) was added to toluene layer (note: for all solutions Au and (R2Se)₂ volume used was constant), and after overnight stirring the solution color changed to yellow. After stirring it overnight, the aqueous layer was discarded and samples were measured via NMR, Raman and XPS.

Synthesis of Gold NPs. For one-phase BSM the modified one-step synthesis² was used. 1 mmol (0.704 ml, 0.1329 M) of HAuCl₄ aqueous solution was dissolved in 20 mL THF. After stirring

for 30 min in ice bath, 0.5 mmol of $(C_8Se)_2$, was added to the solution and stirred for another 2 hours. While keeping the stirring solution in ice bath, 10 mmol of $NaBH_{4aq}$ (in 5 ml of H_2O) was added and stirred for 3 hours. The solution turned to black color immediately. After that, it was rotary evaporated at room temperature and then a large amount of ACN was added. The mixture was stored overnight in a refrigerator. NPs were collected by filtering through a micropore filter system, and washed with ACN. The collected NPs were re-dissolved in toluene, and centrifuged at 14.5K rpm for 1h twice. The top layer was collected and prepared for TEM. For selenium system, first Au NPs were synthesized via modified traditional two-phase procedure,³ with the ratio of 1Au : 3TOAB : 0.5(OctSe)₂ : 10NaBH₄. First 0.15 mmol of TOAB was dissolved in 20 ml of toluene, then 0.05 mmol (0.35 ml, 0.1329 M) of $HAuCl_{4aq}$ was added to the solution. The solution turned to dark red color from clear. When all Au ions were transferred into organic layer, 0.025 mmol $(C_8Se)_2$ was added and stirred for 1-2 hours and the solution turned to dark yellow color. Later, aqueous 5 mmol $NaBH_{4aq}$ (in 5 ml of H_2O) was added to the solution and stirred for 3 hours, while the solution turned to black immediately. The aqueous layer was removed and organic layer was rotary-evaporated. Large amount of acetonitrile (ACN) was added and stored in the refrigerator overnight. Next day, the NPs were micropore filtered, re-dissolved in toluene, and centrifuged for 1h at 14.5K rpm.

Supporting Figures:

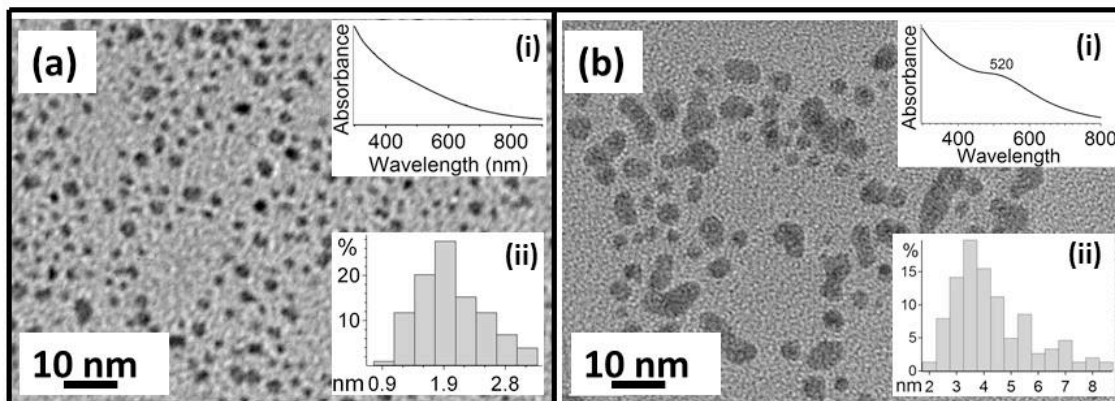


Fig. S1. TEM images of octaneselenoate-stabilized Au NPs synthesized by (a) one-phase and (b) two-phase BSM syntheses. The insets are: (i) UV-vis spectra and (ii) the respective size distributions that give the average size of $2.0 \text{ nm} \pm 0.5 \text{ nm}$ for the former (a) and $4.2 \text{ nm} \pm 1.6 \text{ nm}$ for the latter (b) (Note: both after centrifugation).

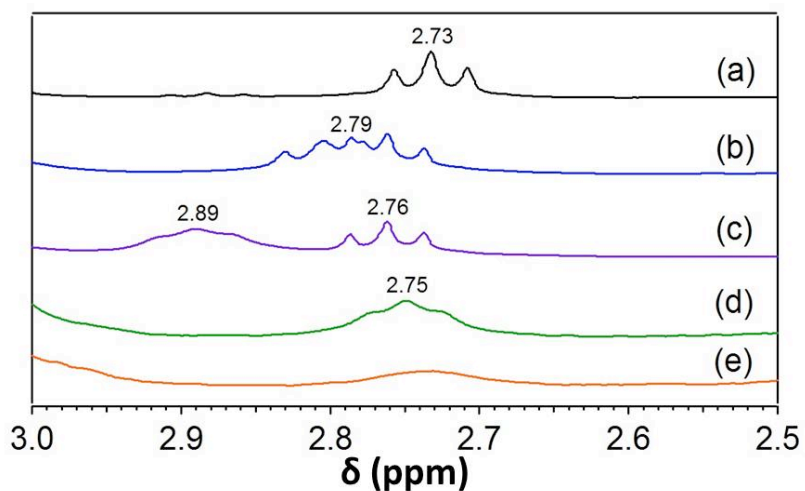


Fig. S2 Enlarged zone of ^1H NMR spectra of (a) 3 TOAB + 0.5 $(\text{C}_8\text{Se})_2$, (b) 1 TOAB + 1 HAuCl_4 + 0.5 $(\text{C}_8\text{Se})_2$, (c) 1.25 TOAB + 1 HAuCl_4 + 0.5 $(\text{C}_8\text{Se})_2$, (d) 2 TOAB + 1 HAuCl_4 + 0.5 $(\text{C}_8\text{Se})_2$, and (e) 3 TOAB + 1 HAuCl_4 + 0.5 $(\text{C}_8\text{Se})_2$ in C_6D_6 .

Table S1. XPS binding energies of (a) solid (C12Se)₂, (b) one-phase intermediate with 1Au : 0.5(C8Se)₂, (c) two-phase intermediate with 3TOAB : 1Au : 0.5(C8Se)₂, and (d) two-phase intermediate with 2TOAB : 1Au : 0.5(C8Se)₂.

(a) (C12Se)₂			(b) 1Au : 0.5(C8Se)₂		
Run	Se 3d		Run	Au 4f	Se 3d
1	55.35		1	84.1	58.25
2	55.35		2	84.3	58.55
3	55.25		3	84.4	58.65
			4	84.2	58.15
	Average (eV)	55.3		84.25	58.4

(c) 3TOAB : 1Au : 0.5(C8Se)₂			(d) 2TOAB : 1Au : 0.5(C8Se)₂		
Run	Au 4f	Se 3d	Run	Au 4f	Se 3d
1	84.2	57.75	1	84.5	58.05
2	84.2	57.85	2	84.4	57.85
3	84.2	58.35	3	84.2	58.25
	Average (eV)	84.2	84.3	57.98	58.05

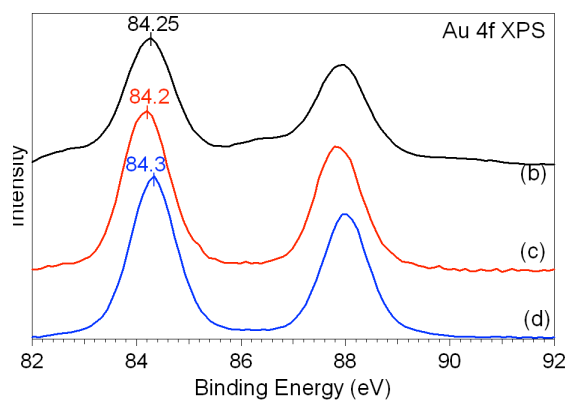
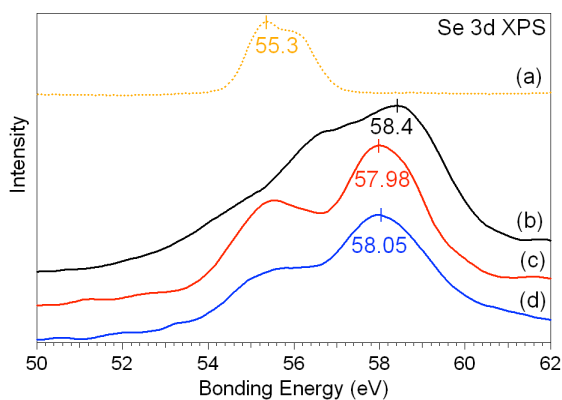


Table S2. DFT calculated vibrational frequencies for reference molecules

Compound	Frequency (cm⁻¹)	Assignment
AuCl₄⁻	261.6	Au-Cl symm. stretch (2 in, 2 out)
	297.6	Au-Cl symm. stretch (all 4)
	321.5	Au-Cl assym. stretch (doubly degenerate, opposite Cl stretch)
HAuCl₄	272.4	Au-Cl symm. stretch (2 in, 2 out)
	309.8	Au-Cl symm. stretch (all 4)
	344	Au-Cl assym. stretch (2 of 4, opposite)
	348.5	Au-Cl assym. stretch (2 of 4, opposite)
	351	Au-Cl assym. stretch (looks like 344)
(C₈H₁₇Se)₂	267.3	Se-Se stretch
	310.6	Se-Se stretch (coupled)
	346.3	Se-Se stretch (coupled)

Table S3. Partial DFT calculated vibrational frequencies for Cl₂AuSe(C₈H₁₇)Cl₂ complex

Complex	Frequency(cm⁻¹)	Assignment
Cl₂AuSe(C₈H₁₇)Cl₂	158	Au-Se stretch
	284.9	Se-Cl stretch
	299.6	Se-Cl stretch
	307.7	Au-Cl stretch
	316.7	Se-Cl stretch
	360.9	Au-Cl ₂ assym. stretch

Table S4. Some representative DFT calculated vibrational frequencies for X₂AuSe(C₈H₁₇)X-OH complexes.

Complex	Frequency (cm ⁻¹)	Assignment
Br₂AuSe(C₈H₁₇)OHBr	102.5	Au-Se stretch
	110	Au-Se stretch
	194.6	Au-Br symm. stretch
	207.4	Au-Br symm. stretch
	258.8	Au-Br asymm. stretch
	255.9	Se-Br stretch
	682.9	Se-OH stretch
Br₂AuSe(C₈H₁₇)OHCl	107.5	Au-Se stretch
	117.3	Au-Se stretch
	199.9	Au-Br symm. stretch
	205.3	Au-Br symm. stretch
	259.6	Au-Br asymm. stretch
	284.7	Se-Cl stretch
	686.6	Se-OH stretch
ClBrAuSe(C₈H₁₇)OHBr	102.7	Au-Se stretch
	110.6	Au-Se stretch (coupled)
	181.9	Se-Br stretch
	207.2	Se-Br stretch
	211.2	Se-Br stretch
	233.4	Se-Br stretch
	292.6	Au-Cl stretch
	309.7	Au-Cl stretch (coupled)
685.9	Se-OH stretch	
ClBrAuSe(C₈H₁₇)OHCl	107	Au-Se stretch
	114	Au-Se stretch
	234.8	Au-Br stretch
	287.2	Se-Cl stretch
	291.8	Se-Cl stretch (coupled)
	310.2	Au-Cl stretch
	341.8	Au-Cl stretch (coupled)
	688	Se-OH stretch
Cl₂AuSe(C₈H₁₇)OHBr	115.5	Au-Se stretch
	215.9	Se-Br stretch
	288.8	Au-Cl stretch
	324	Au-Cl stretch
	350.7	Au-Cl ₂ asymm. stretch
	675.5	Se-OH stretch
Cl₂AuSe(C₈H₁₇)OHCl	116.5	Au-Se stretch
	139	Au-Se stretch
	237.1	Se-Cl stretch (coupled)
	282.5	Au-Cl stretch
	289	Se-Cl stretch
	304.3	coupled Au-Cl, Au-Se, Se-Cl stretch
	318.6	Au-Cl ₂ stretch (coupled)
	350.7	Au-Cl ₂ asymm. stretch
	681.6	Se-OH stretch

Table S5. Proton Numbers of the (C₈Se)₂ per [TOA]⁺ for ratios (a) 1 TOAB + 0.5 (C₈Se)₂, (b) 3 TOAB + 0.5 (C₈Se)₂, (c) 1 TOAB + 1 HAuCl₄ + 0.5 (C₈Se)₂, (d) 1.25 TOAB + 1 HAuCl₄ + 0.5 (C₈Se)₂, (e) 2 TOAB + 1HAuCl₄ + 0.5 (C₈Se)₂, and (f) 3 TOAB + 1HAuCl₄ + 0.5 (C₈Se)₂ C₆D₆.

Sample*	Ratio	
	α -CH ₂ -N ⁺	CH ₂ -Se-Se-CH ₂
(a) 3TOAB : 0.5(C ₈ Se) ₂	8	1.5
(b) 1TOAB : 1Au : 0.5(C ₈ Se) ₂	8	1.6
(c) 1.25TOAB : 1Au : 0.5(C ₈ Se) ₂	8	1.1
(d) 2TOAB : 1Au : 0.5(C ₈ Se) ₂	8	1
(e) 3TOAB : 1Au : 0.5(C ₈ Se) ₂	8	0.5

*Note: The numbers of protons for all samples in α -CH₂-N⁺ from TOA⁺ was assigned as 8.

Table S6. Cartesian coordinates (XMol format, Angstroms) for optimized structures of 19 species calculated at the B3LYP/cc-pVDZ level of theory.

AuCl₄-

5

Au	-0.0000000852	-0.0000018642	0.0000048638
Cl	0.0000000185	-2.2358980954	-0.7145700726
Cl	-0.0000000216	2.2361835796	0.7137033507
Cl	-2.3475429180	-0.0001384856	0.0004227930
Cl	2.3475434012	-0.0001364985	0.0004165326

References:

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3. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R., Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid-Liquid system. *Journal of the Chemical Society, Chemical Communications* **1994**, (7), 801-802.