

Supporting Information For

9-BBN Induced Synthesis of Nearly Monodisperse ω -Functionalized Alkylthiol Stabilized Gold Nanoparticles

Rajesh Sardar and Jennifer S. Shumaker-Parry^{*}

Department of Chemistry, University of Utah, 315 South 1400 East, RM 2020, Salt Lake City, Utah 84112
shumaker-parry@chem.utah.edu

Chemicals. Chloro(triethylphosphine) gold(I) (97%), silver heptafluorobutyrate (97%), palladium acetate (98%), potassium tetrachloroplatinate(II) (98%), 1-octadecanethiol (ODT, (98%), trioctylamine (TOA, 98%), 0.5 M THF solution of 9-Borabicyclo[3.3.1]nonane (9-BBN), 11-mercaptoundecanoic acid (MUA, 99%) and 11-mercapto-1-undecanol (MUOH, 99%) were purchased from Aldrich. 11-mercaptoundecanamide (MUDA, 99%) and azide-terminated undecyl disulfide (AUDDS, 99%) were obtained from Asemblon (Redmond, WA). HPLC grade toluene and ethanol were obtained from Fisher Scientific. All chemicals and solvents were used as received without additional purification. The glassware used in the synthesis was cleaned with aqua-regia, rinsed copiously with nanopure water, and dried overnight prior to use. All reactions were carried out in air.

Spectroscopy and microscopy measurements. Absorption spectra (300 nm to 800 nm) were collected using a Perkin-Elmer Lambda 19 UV/Vis/NIR spectrophotometer. Transmission Electron Microscopy (TEM) micrographs were obtained using a Tecnai-12 instrument operating at 100 KV accelerating voltage. Before the TEM sample preparation, the sample was centrifuged at 4000 r.p.m for 10 minutes to remove any large aggregates. From the centrifuged solution, one drop of reaction mixture was deposited on a 150-mesh formvar-coated copper grid, and excess solution was removed by wicking with filter paper to avoid particle aggregation. The grid was then allowed to dry before being imaged. Particle size analysis was conducted by analyzing at least 200 particles in the TEM images using Scion Image Beta 4.02 Software. In Scion Image, after setting the known distance and unit, the 'Analyze Particle' parameter was used to generate a table of particle diameters. This table was then exported into Microsoft Excel 2003 for statistical analysis. In a similar way, we calculated the interparticle spacing by analyzing a minimum of 150 interparticle spacings. In the FTIR analysis, approximately 2 mg of dry solid samples were mixed with 100 mg of pregrind KBr and a minipress was used to prepare a transparent film.

Synthesis of ODT capped gold nanoparticles. 0.017 gm (0.05 mmol) of Et₃PAuCl was dissolved in 100-mL toluene in air at room temperature. The solution was stirred for 5 minutes and at this point 0.17 mL (0.5 mmol) of ODT was injected and stirring was continued for another 30 minutes. Then 0.2 mL of 0.5 M 9-BBN in THF was added followed by immediate injection of 0.005mL (0.01 mmol) of TOA. The color of the solution gradually changed from light purple to purple and at the end of 65 minutes after the addition of 9-BBN, it was reddish-purple color. The stirring was stopped

and the solution was centrifuged to remove any large aggregates. One drop of the centrifuged solution was deposited on the formvar grid and analyzed by TEM.

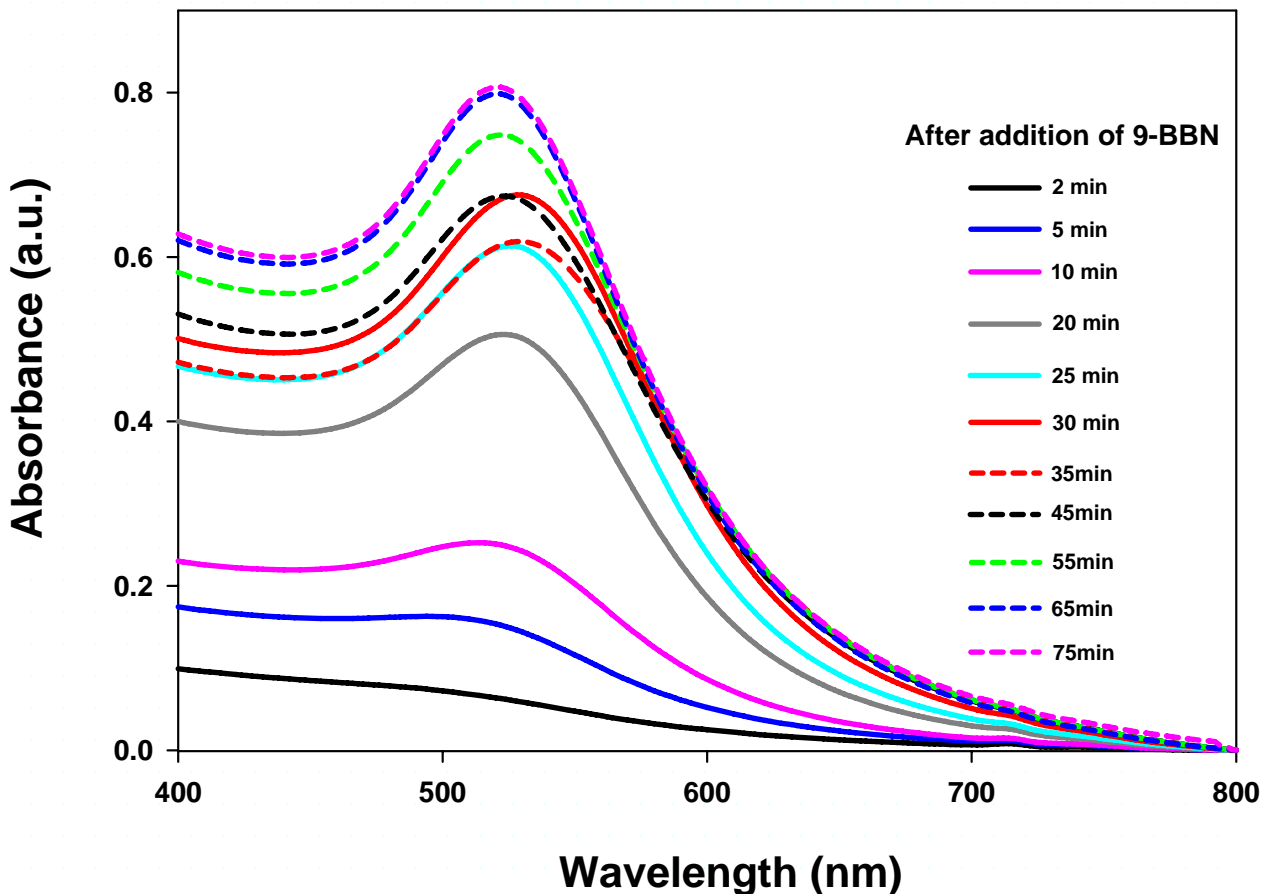
Synthesis of functionalized AuNPs. In the synthetic procedure, 0.017 gm (0.05 mmol) of Et_3PAuCl was dissolved in 100-mL toluene in air at room temperature. The solution was stirred for 5 minutes and at this point 0.066 gm (0.3 mmol) of 11-mercaptoundecanoic acid (MUA) was added and stirring was continued for another 30 minutes. The solution was heated until the temperature reached 60°C . At this point, 0.6 mL of 0.5 M 9-BBN in THF and 0.010 mL (0.02 mmol) of TOA were added to the reaction mixture. Immediately after addition of 9-BBN, the color of the solution changed to orange followed by light purple and within 10 minutes it was a reddish-purple colored suspension. The solution was heated for another 10 minutes and then removed from heat and stirred at room temperature for 30 minutes. The solution was centrifuged resulting in a reddish-purple colored solid. The solid was dried under nitrogen for further analysis. 5 mg of solid was redissolved in 50-mL of ethanol and analyzed by UV-visible spectroscopy and TEM. The solid also was analyzed by FTIR to determine the nature of the functional group as well as the oxidation state of gold. Under similar reduction conditions and identical molar ratios of gold salt and 9-BBN, reduction reactions were performed in the presence of 11-mercapto-1-undecanol (MUOH), 11-mercaptoundecanamide (MUDA), and azide-terminated undecyl disulfide (AUDDS).

Synthesis of TOA stabilized silver nanoparticles. At room temperature, a clear homogeneous solution of 0.016 gm (0.05 mmol) of silver heptafluorobutyrate was prepared in 100-mL of toluene. In the solution, 0.13 mL (0.3 mmol) of trioctylamine was injected and the solution was stirred for 30 minutes. At this point, 0.05 mL of 0.5 M 9-BBN solution in THF was injected. After the addition of 9-BBN, the color of the solution was light yellow which became more intense over the period of 1h of stirring at room temperature. The final solution was dark yellow and displayed a sharp peak (λ_{max}) at 408 nm in the UV-visible spectroscopy absorption spectrum. The solution was centrifuged and one drop was deposited on a formvar grid for TEM analysis.

Synthesis of ODT capped palladium nanoparticles. 0.011 gm (0.05 mmol) of $\text{Pd}(\text{OAc})_2$ was dissolved in 100-mL of toluene which produced a light yellow colored homogeneous solution with a distinct peak (λ_{max}) at 398-nm in the UV-visible absorption spectrum. Into this solution, 0.13 mL (0.3 mmol) of TOA was added and the solution was heated to 60°C for 30 minutes. After addition of TOA, the color of the solution became dark yellow and the peak in UV-visible spectra at 398-nm disappeared and a new peak (λ_{max}) at 340-nm appeared, which could be due to the formation of some palladium-amine complex. At this point, 0.4 mL of 0.5 M THF solution of 9-BBN was injected. After addition of 9-BBN, the color of the solution slowly changed from dark yellow to light brown and over the course of 2 hrs of heating, the solution was dark brown. As the solution was cooled down to room temperature, the brown solid precipitated out. The solution was centrifuged. The solid was redispersed in toluene in the presence of 0.3 mmol of ODT with stirring at room temperature for 2hrs. At this point, most of the solid was dispersed in solution which became a dark brown color with no absorption maxima in the UV-visible spectrum. The solution was centrifuged to remove undissolved solid and from one drop of solution was deposited on a formvar grid for TEM analysis.

Synthesis of TOA stabilized platinum nanoparticles. 0.021 gm (0.05 mmol) of K_2PtCl_4 was transferred to a glass vial and 10-mL of DMF was added. The sample was then sonicated at room temperature until all of the solid dissolved, producing a light orange colored homogeneous solution.

The solution was then transferred to a 250-mL erlenmeyer flask, diluted to 100-mL by adding 90-mL of toluene, and stirred for 30 minutes at 80 °C. At this point, 0.13 mL (0.3 mmol) of TOA was added and the solution was stirred for 30 minutes. Then 0.4 mL of 0.5 M 9-BBN in THF was injected. Heating was continued for 8 hrs at 80 °C with constant stirring. After heating for 8 hrs, the solution was yellowish-brown. The solution was centrifuged to remove any large aggregates. One drop of the solution was deposited on a formvar coated carbon grid for TEM analysis.

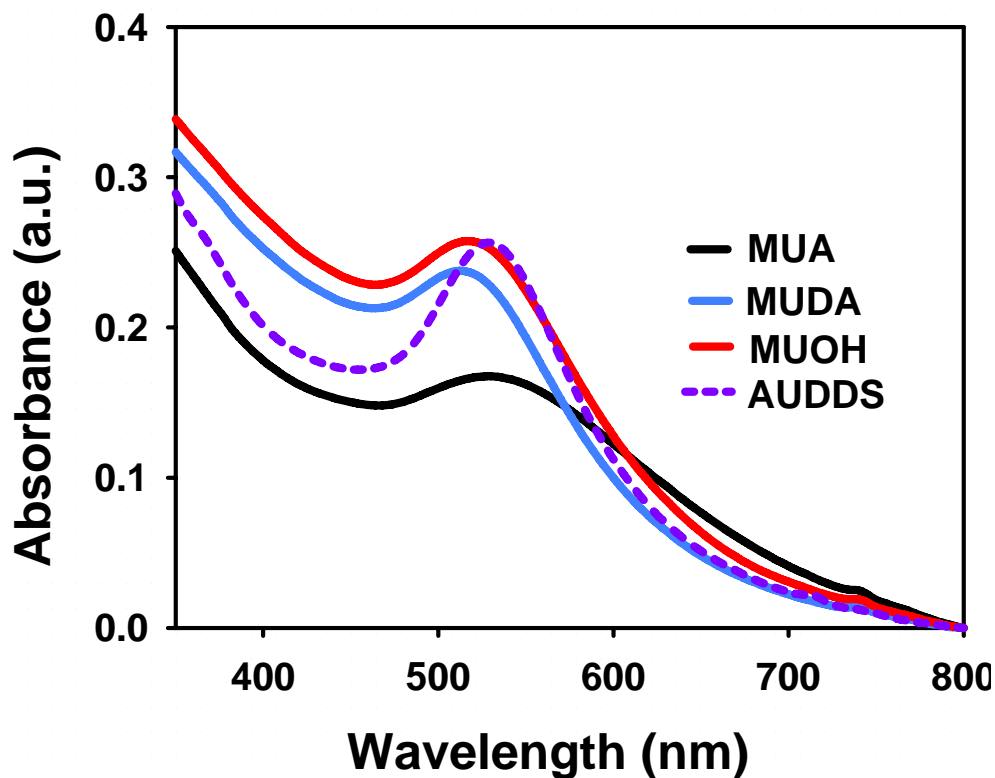


SI-Figure 1. UV-visible absorption spectra of ODT capped AuNPs at different time intervals during the synthesis.

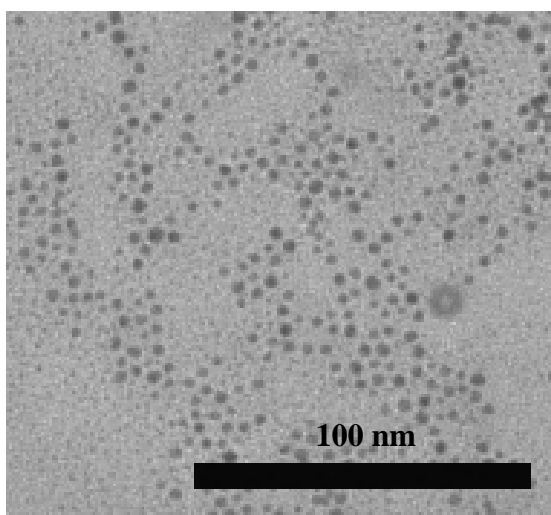
SI-Table 1. Comparison of UV-visible absorption maxima and size of gold nanoparticles synthesized in the presence of different ω -functionalized alkylthiols.^a

Samples	UV-visible absorption maximum (λ_{max}) nm	Particle size, nm ^b
AuNPs-MUA	528	1.9 (0.3)
AuNPs-MUDA	512	1.4 (0.2)
AuNPs-MUOH	517	2.0 (0.3)
AuNPs-AUDDS	529	2.2 (0.3)

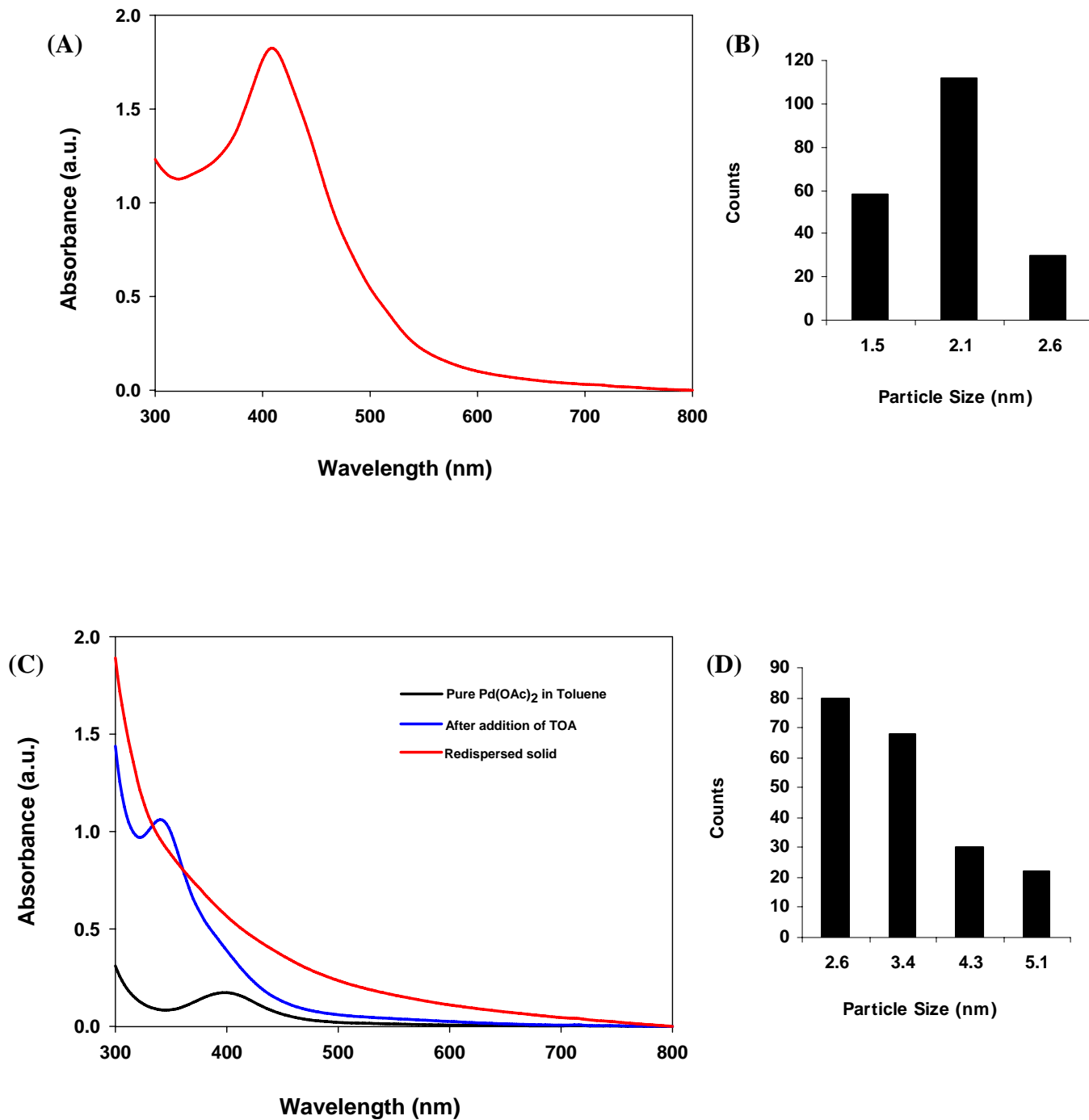
^aIn each case, at least 200 particles were counted to determine the size and the dispersity. ^bThe number in parenthesis indicates the standard deviation.



SI-Figure 2. UV-Vis absorption spectra of AuNPs in the presence of different ω -functionalized alkylthiols.



SI-Figure 3. TEM image of MUOH capped AuNPs synthesized using 9-BBN as a reducing agent.



SI-Figure 4 The UV-visible absorption spectra of (A) AgNPs and (C) PdNPs and histogram of particle size analysis for (B) AgNPs and (D) PdNPs.