Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

Surface versus Solution Chemistry: Manipulating Nanoparticle Shape and Composition through Metal-Thiolate Interactions

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Chemicals

Gold (III) chloride trihydrate ($HAuCl_4$•$3H_2O$, ≥ 99.9%, Lot# MKCC8511), L-ascorbic acid (L-AA, BioUltra, ≥ 99.0%, Lot# SLBS0713V), hexadecyltrimethylammonium bromide (CTAB, BioUltra, ≥ 99.0%, Lot# BCBT1510), sodium citrate tribasic dihydrate (Na_3Citrate•$2H_2O$, BioUltra, ≥ 99.5%, Lot# BCBR9536V), sodium borohydride ($NaBH_4$, 99.99%, Lot# MKBW6321V), 4-methylthiophenol, (98%, Lot# MKVP564SV), thiophenol (99%, Lot# 33596DMV), 4-triflouromethylthiophenol, aniline (99.5%, Lot# SHBH0581V), 1-dodecanethiol (98%), dodecylamine (98%), and palladium (II) chloride ($PdCl_2$, ≥ 99.9%, Lot# MKBV5028V) were purchased from Sigma Aldrich. 4-hydroxythiophenol (97%, Lot# 10198402) was purchased from Alfa Aesar. 4-cholorthiophenol (Lot# S6885244607) was acquired from Merck and 4-aminothiophenol (98%, Lot# 34JFM-SG) and 2-aminthiophenol (95%, Lot# W8Y4L-SS) were obtained from TCI America. Acetone (ACS grade), chloroform ($CHCl_3$, ACS grade), hydrochloric acid (HCl, 1.0 Normal), methanol (ACS grade) and isopropanol (ACS grade) were purchased from Macron. All chemical were used as received without further purification. All vials were rinsed with ethanol and dried with air prior to use. Milli-Q nanopure water (18.2 MΩ•cm) was used in all experiments.

Characterization.

Samples for scanning electron microscopy (SEM) were prepared by drop-casting a dispersed particle solution onto a cleaned Si wafer. After the solvent evaporated, the Si wafers were washed with methanol several times to remove excess surfactant. Images were obtained with a FEI Quanta FEG 600 field-emission environmental SEM operating at 30 kV with a spot size of 3 with secondary electron detection.

For transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), a dispersed particle solution was drop-casted on a 300 mesh Cu grid (Ted-Pella, Formvar removed by dipping grid in chloroform). After 5 minutes, the grid was dipped in methanol, air dried for 30 minutes and then soaked in acetone overnight. Sample analysis by STEM were conducted on a JEOL JEM 3200FS TEM, equipped with a Gatan 4k x 4k UltraScan 4000 CCD camera, operating at 300 kV with a spot size of 1. Energy dispersive X-ray spectroscopy (EDS) spectra were all obtained with an Oxford Instruments X-maxN 100 TLE silicon drift detector (SDD) interfaced to the JEOL JEM 3200FS TEM using the AZtec software package. Elemental mapping was conducted in STEM-EDS mode.

Electrostatic potential approximations were computed through Spartan software with Hartree-Fock method and the 6-31G* basis set. All values were calculated in the gas phase and were used as given.

Inductively coupled plasma mass spectrometry was performed in conjunction with the University of Illinois Microanalysis center. Samples were centrifuged 3 times at 15000 rpm for 10 minutes to remove excess surfactant and free thiol or metals. Samples were digested by Discovers SPD (CEM) Mircrowave digester with an aqua regia acid mixture. Samples were analyzed using a NexION 350D.

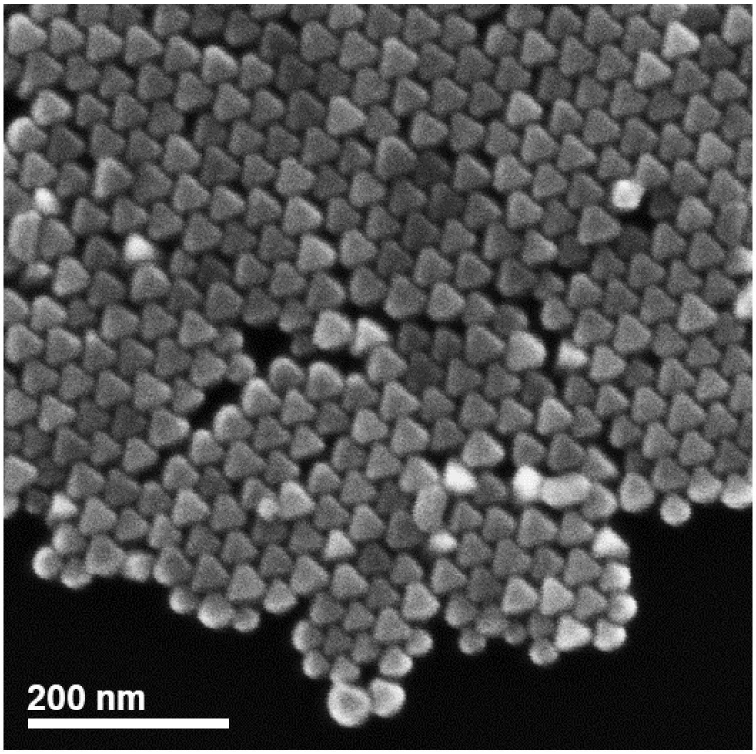
Synthesis of Gold Octahedra:

Octahedra were synthesized by a previously reported hydrothermal method in a 30 mL vial.[1] A growth solution of .250 mL of 10 mM $HAuCl_4 \cdot 3H_2O$, 1.5 mL of 100 mM CTAB, and .050 mL of 100 mM Na_3Citrate were diluted with 8.2 mL of water. Solutions were inverted and allowed to mature in an oil bath at 110 °C over night. Au octahedra were collected by centrifugation (10,000 rpm / 12,000 g) after 15 minutes and diluted to a volume of 3 mL with water.

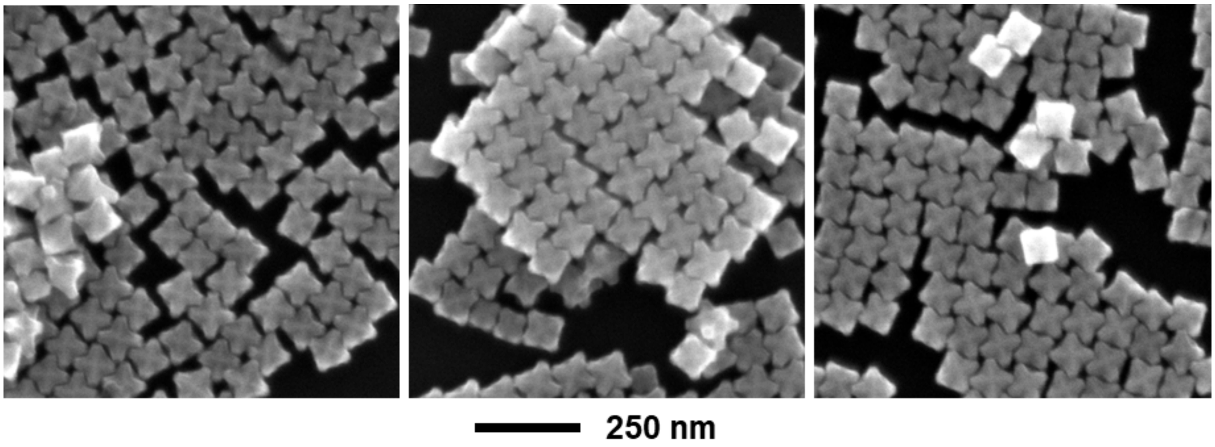
Seed-Mediated Co-Reduction (SMCR):

SMCR was performed as previously described with minor modifications.[2] A growth solution containing 21.3 mL of H_2O, 1 mL of 200 mM CTAB, 0.1 mL of 100 mM $HAuCl_4 \bullet 3H_2O$, and 0.1 mL of 10 mM H_2PdCl_4 were added to a 30 mL reaction vial. The solutions were gently inverted and 1.5 mL of freshly prepared 100 mM L-AA was added. Quickly, 1 mL of additive in 200 mM CTAB was introduced and the reaction was inverted twice. To this solution, a 1 mL of Au octahedra were added. After the addition of the Au seeds, the reaction vial was inverted twice and placed in an oil bath at 25°C overnight. The stellated Au/Pd nanostructures were collected by centrifugation (10,000 rpm / 12,000 g) after 15 minutes and diluted to a volume of 1 mL with water.

Supplemental Figures:



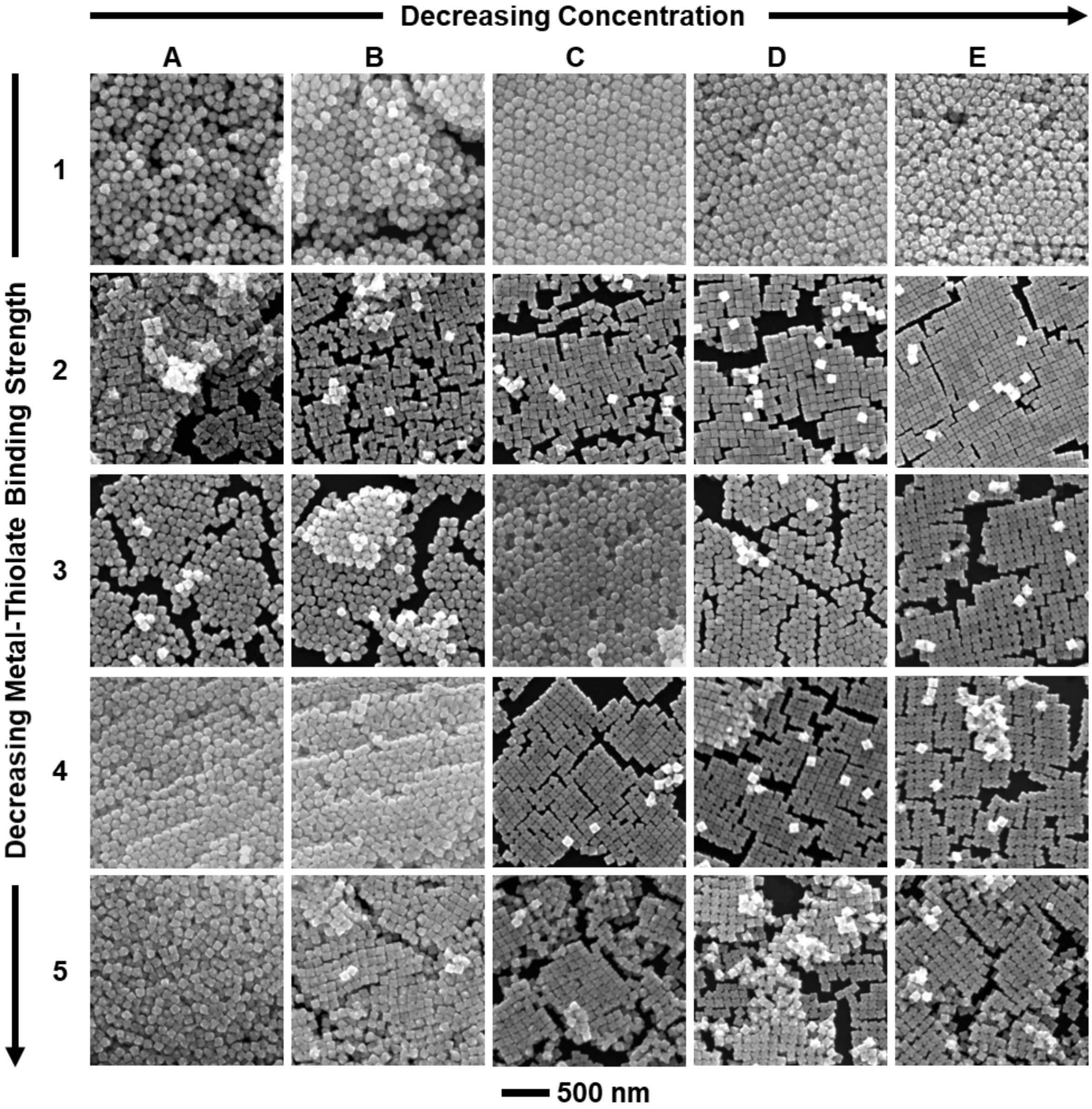
Supplemental Figure 1. SEM of synthesized Au octahedra used as seeds in SMCR.



Supplemental Figure 2. SEM of separate batches of Au/Pd octopods prepared without the addition of aromatic thiols.

Surface Facet	Thiolate	Binding Strength	Method, Binding Motif	Ref.
{111}	4-ATP	-91.8 kcal/mol	DFT, Bridge	3
{111}	4-MTP	-88.2 kcal/mol	DFT, Bridge	3
{111}	TP	-85.2 kcal/mol	DFT, Bridge	3
{111}	4-CTP	-82.3 kcal/mol	DFT, Bridge	3
{111}	4-FTP	-76.5 kcal/mol	DFT, Bridge	3
{111}	Metylthiolate	-45.9 kcal/mol	DFT, Staple	4
{100}	Metylthiolate	-55.6 kcal/mol	DFT, Staple	4
{110}	Metylthiolate	-59.0 kcal/mol	DFT, Staple	4
{111}	Metylthiolate	-51.7 kcal/mol	DFT, Bridge	4
{100}	Metylthiolate	-54.0 kcal/mol	DFT, Bridge	4
{110}	Metylthiolate	-57.2 kcal/mol	DFT, Bridge	4

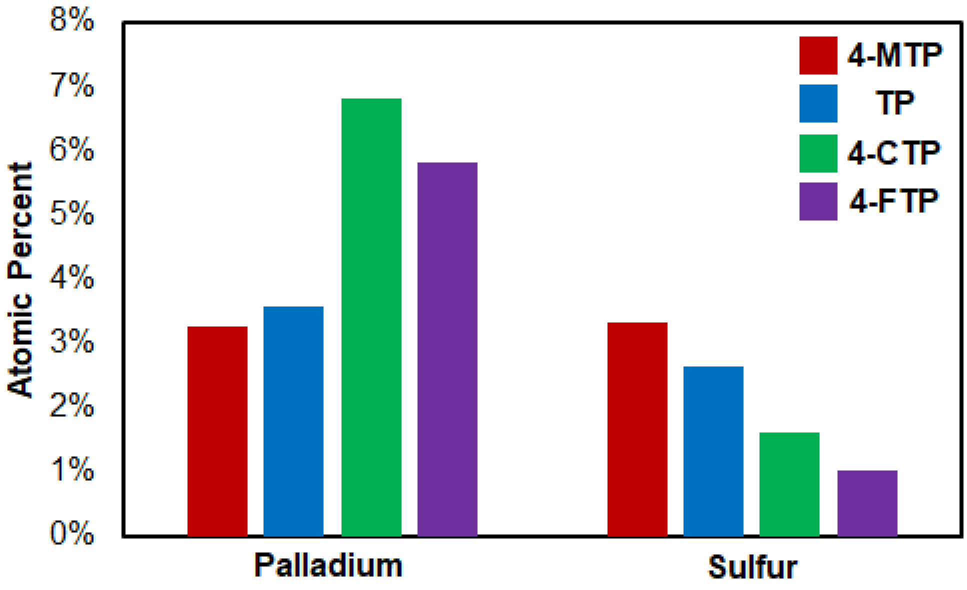
Supplemental Table 1. Calculated binding energies of 4-aminothiophenol (4-ATP), 4-methylthiophenol (4-MTP), thiophenol (TP), 4-cholorthiophenol (4-CTP), 4-trifluoromethyl thiophenol (4-FTP), and methylthiolate on different Au surfaces. These values are from SI references 3 and 4.



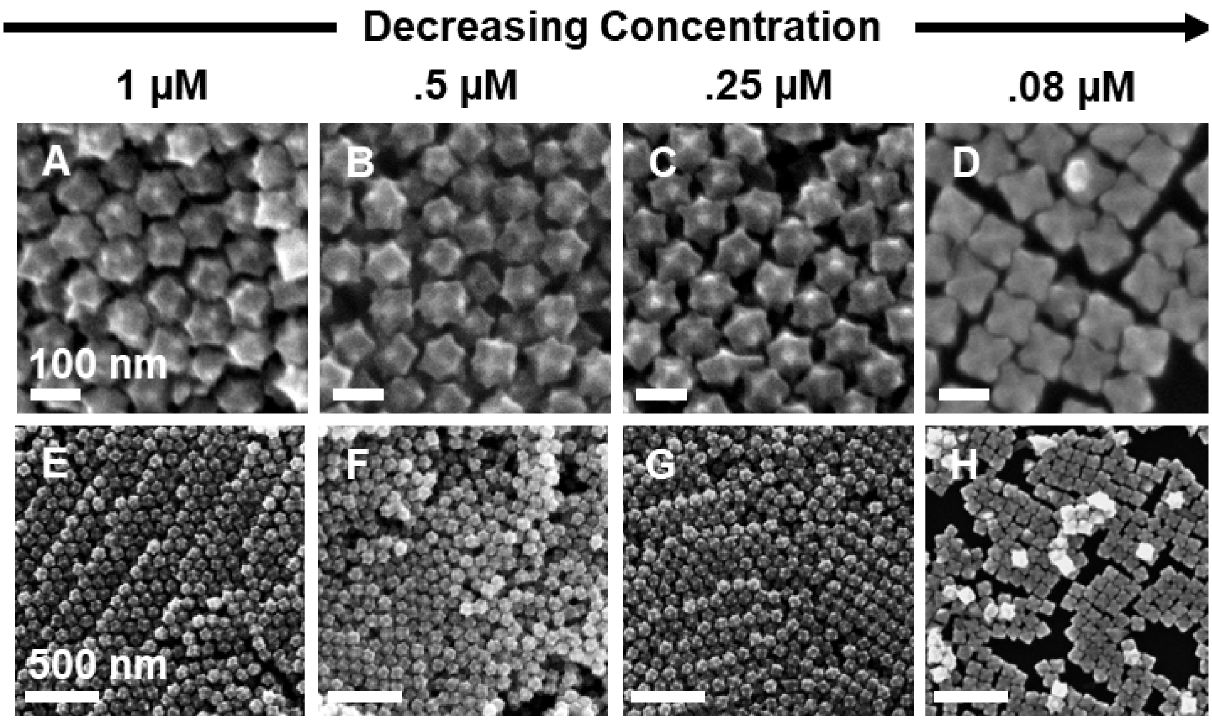
Supplemental Figure 3. Low magnification SEM of 4-aminothiophenol (row 1), 4-methylthiopehnol (row 2), thiophenol (row 3), 4-chlorothiophenol (row 4), and 4-trifluoromethylthiophenol (row 5) at 30 µM (column A), 20 µM (column B), 10 µM (column C), 5 µM (column D), and 1 µM (column E) concentrations.

Additive	Metal	Atomic Percent (%)				
		30 μM	20 μM	10 μM	5 μM	1 μM
4-ATP	**Au**	100	94.0±.5	89.3±0.8	88.3±1.4	88.4±.08
	Pd	0	6.0±.5	10.7±.08	11.7±1.4	11.6±.08
4-MTP	**Au**	100	91.5±1.1	89.6±1.4	90.0±0.8	86.9±1.0
	Pd	0	8.5±1.1	10.4±1.4	10.0±0.8	13.1±1.0
TP	**Au**	100	94.4±1.6	92.9±1.6	90.5±1.5	88.2±1.2
	Pd	0	5.6±1.6	7.1±1.6	9.5±1.5	11.8±1.2
4-CTP	**Au**	92.7±0.8	91.2±06	88.6±1.3	88.2±1.2	91.4±0.6
	Pd	7.3±0.8	8.8±0.6	11.4±1.3	11.8±1.2	8.6±0.6
4-FTP	**Au**	93.9±1.2	91±0.7	90.6±1.8	91.4±1.0	90.8±1.0
	Pd	6.1±.1.2	8.3±.07	9.4±.1.8	8.6±1.0	9.2±1.0

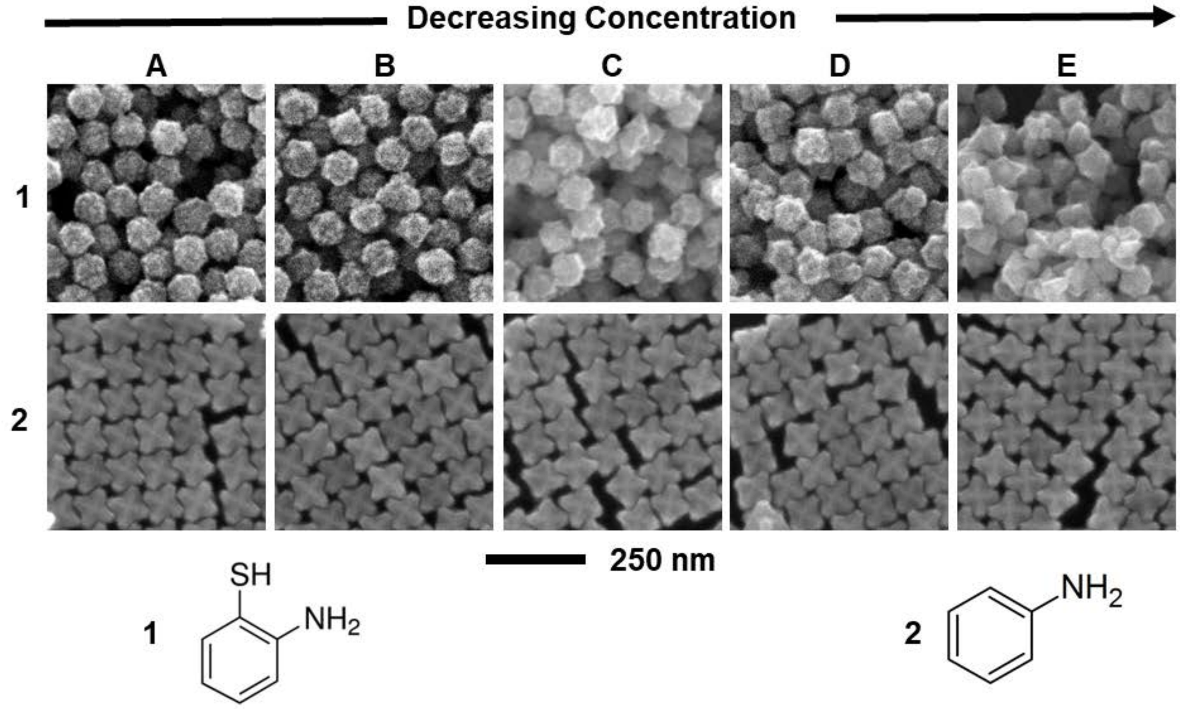
Supplemental Table 2. EDS data with standard deviations for samples presented in Figure 1.



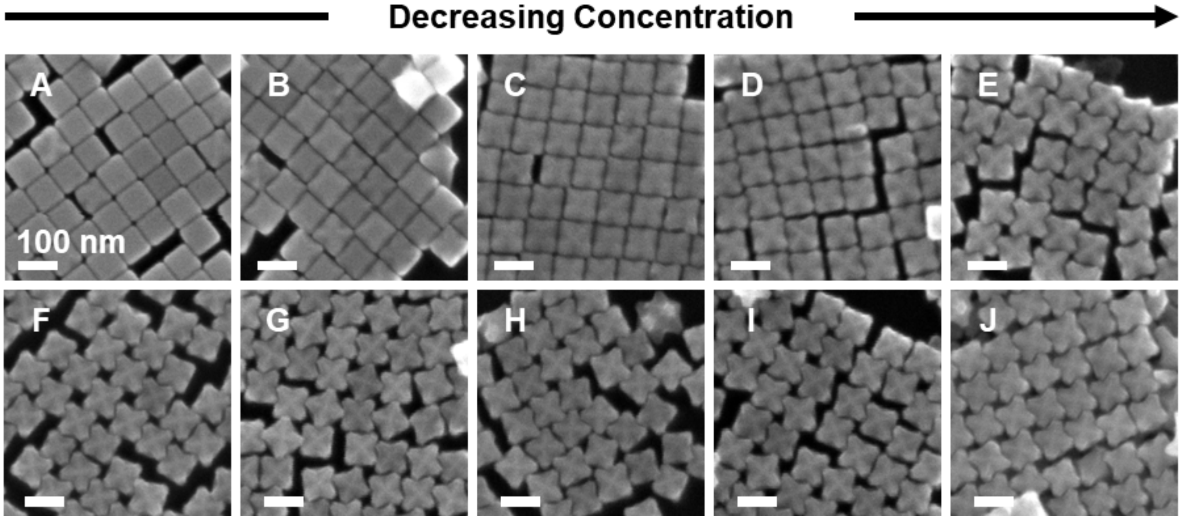
Supplemental Figure 4. Atomic percent of Pd and S in samples prepared with 4-MTP (red), TP (blue), 4-CTP (green), and 4-FTP (purple) obtain by ICP-MS (Samples A2-5 of Figure 2). The percent of Pd was calculated by dividing the moles of Pd by the moles of metal (Au + Pd). The percent S was calculated by dividing the moles of S by moles of metal and sulfur (Au + Pd + S).



Supplemental Figure 5. SEM of small concentrations 4-aminothiophenol with both high and low magnification fields of view.

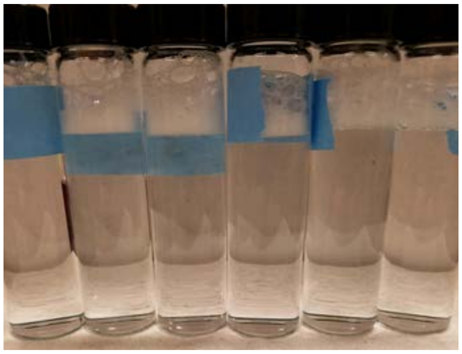


Supplemental Figure 6. SEM of products obtained by adding 2-aminothiophenol (row 1) and aniline (row 2) at 30 µM (column A), 20 µM (column B), 10 µM (column C), 5 µM (column D), and 1 µM (column E) concentrations.

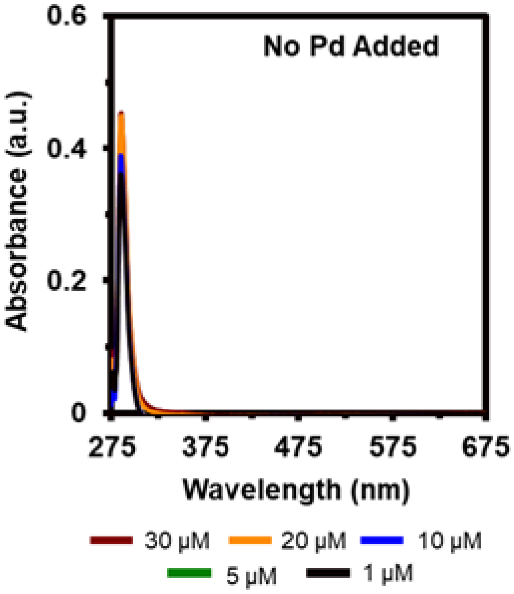


Supplemental Figure 7. SEM of dodecanethiol (a-e) and dodecylamine (f-j) at 30 µM (a,f), 20 µM *b,g), 10 µM (c,h), 5 µM (d,i), and 1 µM (e,j) concentrations.

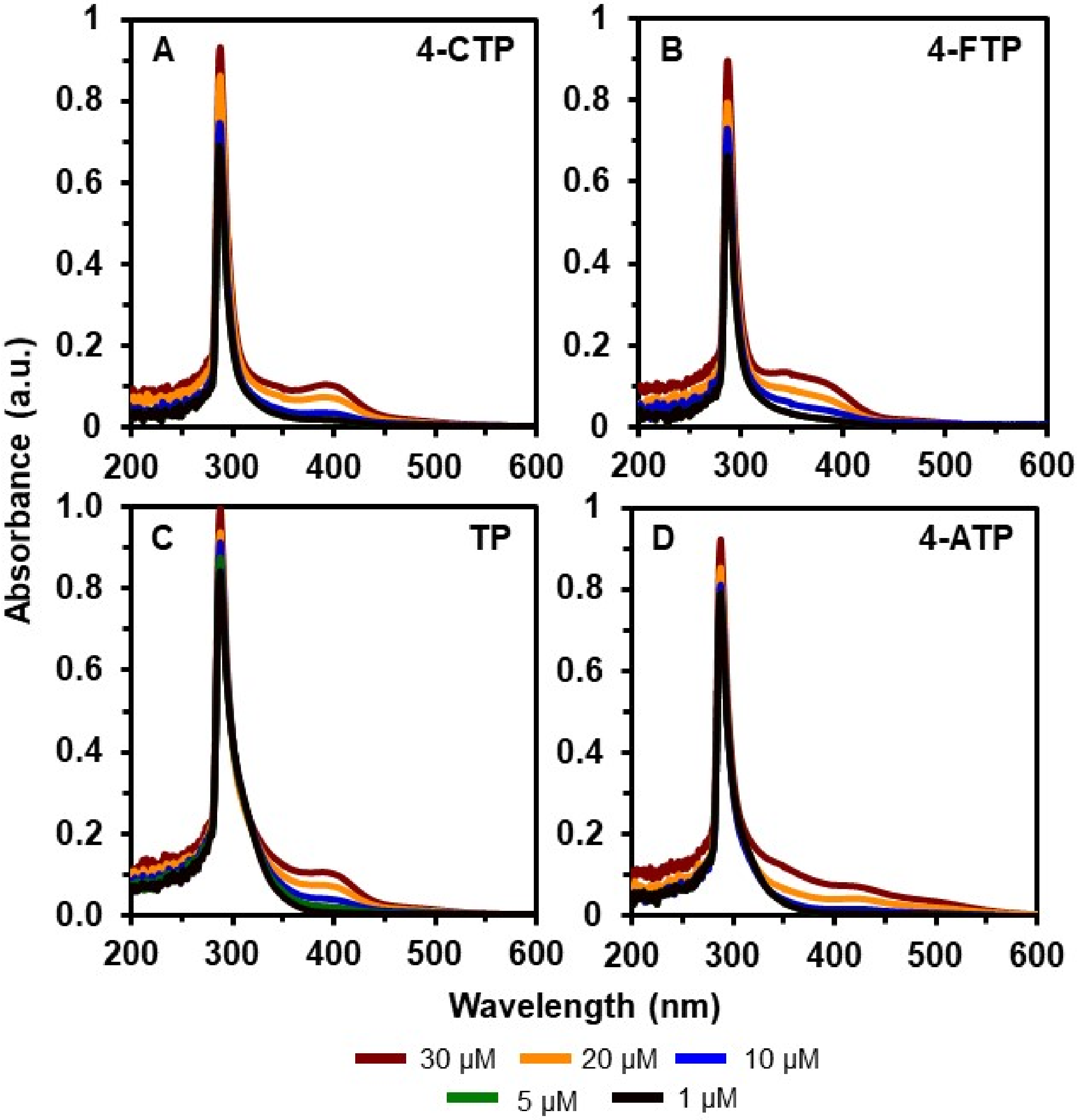
Supplemental Figure 8. Optical images of supernatant obtained from Figure 4 where concentration of thiol is increasing from left to right.



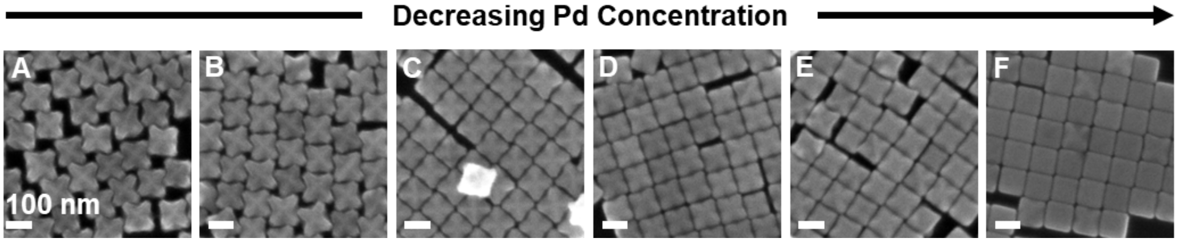
Supplemental Figure 9. Optical images of supernatant obtained from synthesis of branched structures with Au and TP. No Pd was added to these reactions. TP concentrations increase from left to right.



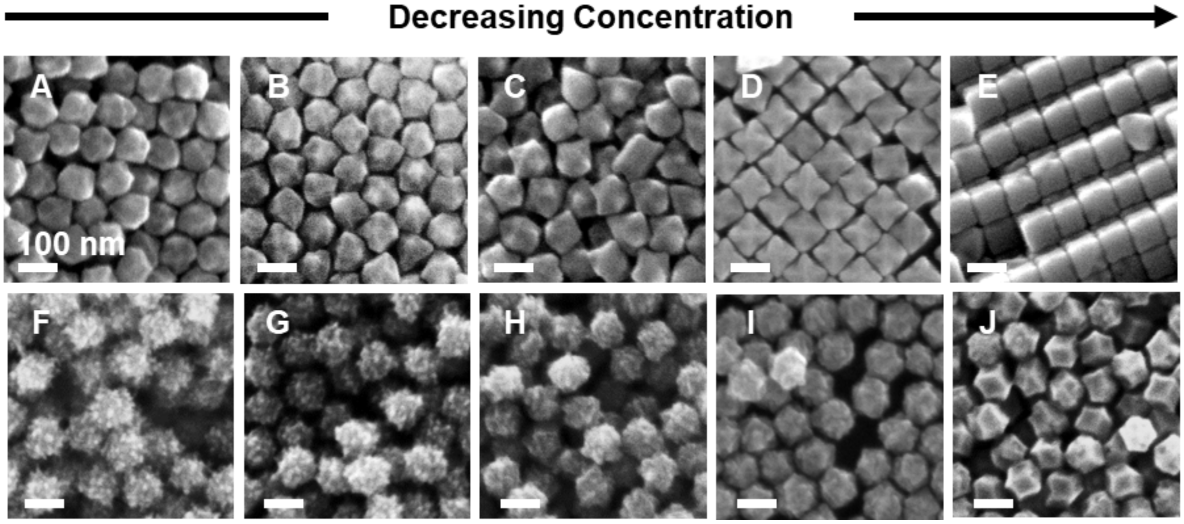
Supplemental Figure 10. UV-visible spectra of supernatant from the synthesis of branched NPs in the presence of TP and absence of Pd precursor.



Supplemental Figure 11. UV-visible spectra of a) 4-CTP, b) 4-FTP, c) TP, and d) 4-ATP at different concentrations of each additive.



Supplemental Figure 12. SEM of products obtained by decreasing the amount of Pd present in the growth solution.



Supplemental Figure 13. SEM of thiophenol (a-e) and 4-aminothiophenol (f-j) at 30 µM (a,f), 20 µM (b,g), 10 µM (c,h), 5 µM (d,i), and 1 µM (e,j) concentrations in the absence of Pd.

References

[1] C. C. Chang, H. L. Wu, C. H. Kuo, M. H. Huang, *Chem. Mater.* **2008**, *20*, 7570

[2] C. J. DeSantis, A. C. Sue, M. M. Bower, S. E. Skrabalak, *ACS Nano* **2012**, *6*, 2617.

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[4] G. Hu, R. Jin and D. Jiang, *Nanoscale*, **2016**, *8*, 20103–20110.