Electronic Supplementary Material (ESI) for Green Chemistry

Supporting information to

Mechanochemical Synthesis of Ultrasmall Monodisperse Amine-Stabilized Gold Nanoparticles with Controllable Size

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1. Experimental Details

Materials and Reagents:

All chemicals and solvents were purchased from commercial sources and used without purification. Hydrogen tetrachloroaurate (III) hydrate was purchased from Strem Chemicals, Inc. Octadecylamine, hexadecylamine, pentadecylamine, DMAP, 4,4'-BIPY, imidazole, benzyl disulfide, citrate, and ω-mercaptododecanoic acid were purchased from Sigma-Aldrich. 400-mesh carbon supported TEM grids were obtained from Electron Microscopy Science. DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as a Maldi-TOF matrix and was purchased from Sigma-Aldrich.

Equipment:

High-resolution TEM and EDAX were performed using a Philips CM200 200 kV TEM. UV–vis spectra were recorded on a Jasco V-660 spectrophotometer. XPS was performed on a VG ESCALAB 3 MKII spectrometer (VG, Thermo Electron Corporation, UK) equipped with an Mg Kα source. PXRD was performed using the Bruker D2 Phaser diffractometer using as CuKα source. A Retsch Mixer Mill MM 400 was used to perform milling experiments. Maldi-TOF MS measurements were performed using the Bruker Autoflex III with a laser source of Nd-YAG UV 355nm and a flight tube of 1.6m in linear mode.

Synthesis of Au NP:

In a typical reaction a 10mL stainless steel milling jar was filled with a total of 0.2000g of solid reagent material where a 1:5 ratio of precursor to ligand would require 0.0403g of HAuCl4 and 0.1597g octadecylamine. To this, two 7mm stainless steel balls were added. For the scale-up experiment, a 25 mL jar was used with 1g of starting material. The jar was then closed and loaded onto the Retsch Mixer Mill. The reaction took place over 90min. at 29.5Hz. At the end of the reaction, the solid product was scrapped out of the jar with a spatula and weighed. The product was suspended in 2mL of toluene and sonicated for 2min. The suspension was then placed next to a supermagnet to remove any free steel shrapnel from the milling process. The solution was decanted, leaving any steel behind with the magnet. TEM sample was taken. All TEM grids were made with mill nanoparticles suspended in toluene and deposited onto a 400-mess carbon supported copper TEM grid. Furthermore, the solution was gently ground with a mortar and pestle, the solvent was pipetted off and passed through a fritted filter. Two more 2mL toluene aliquots were passed through the mortar and pestle with the remaining solid. A sampling of the filtrate is taken for TEM measurements and the toluene is then evaporated off.

Maldi-TOF MS measurements:

Maldi-TOF MS samples were prepared as follows: 10mg of DCTB and 1mg of AuNPs were gently ground with a mortar and pestle for about 5min until the sample appeared homogeneous by eye. The solid was then placed onto the Maldi-TOF sample plate and a 5μL drop of MeOH (HPLC grade) was dropped onto the solid. The solution was allowed to evaporate off and Maldi-TOF measurements were taken in linear positive mode.

2. TEM Data

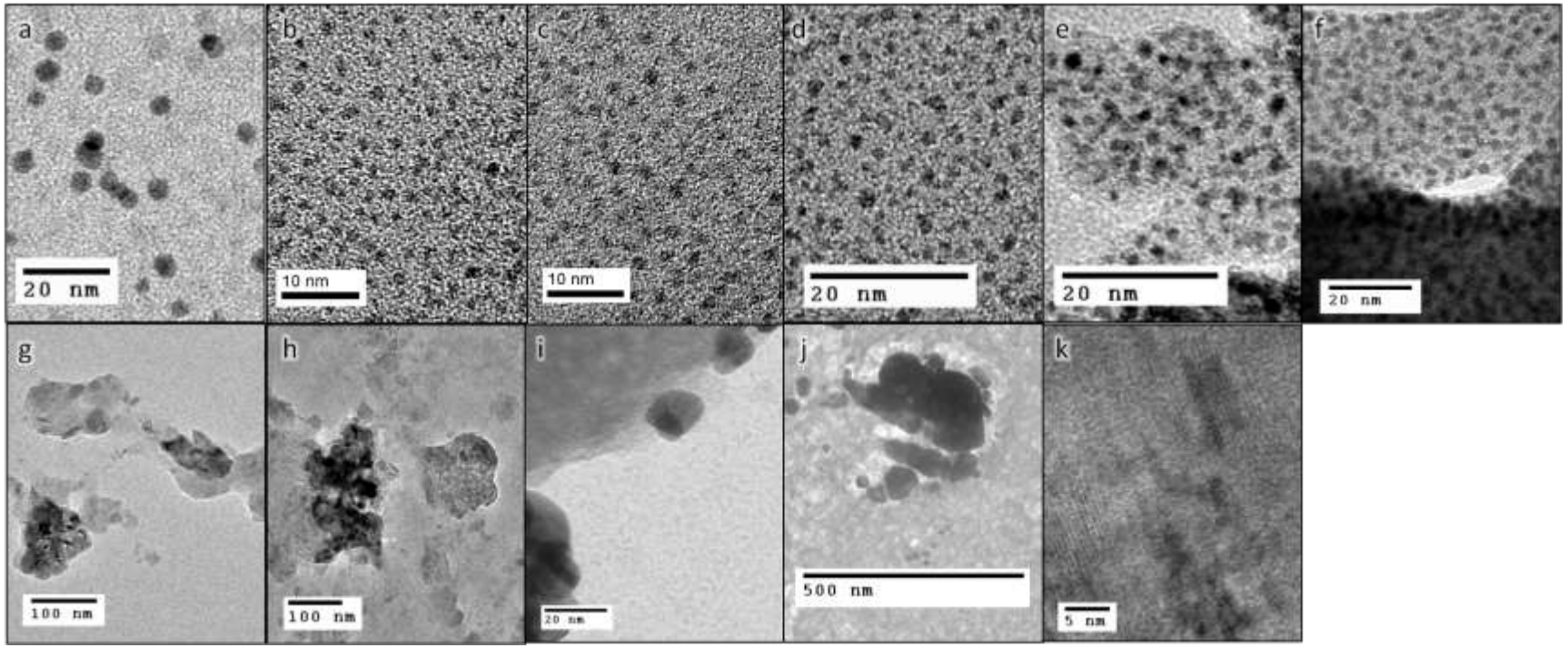
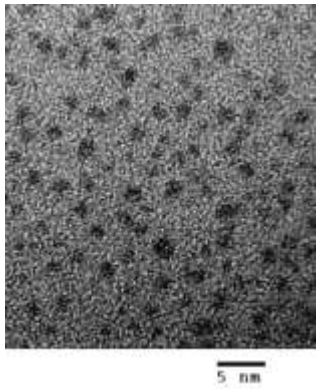


Figure S1: Representative TEM images obtained for the AuNP synthesis with the following ligands: a. pentadecylamine-AuNPs, b. hexadecylamine-AuNPs, c. heptadecylamine-AuNPs, d. octadecylamine-AuNPs, e. DMAP-AuNPs, f. 4,4'-BIPY-AuNPs, g. imidazole-AuNP, h. 1-methylimidazole-AuNPs, i. benzyl disulfide-AuNPs, j. citrate-AuNP, k. ω-mercaptododecanoic acid-AuNP



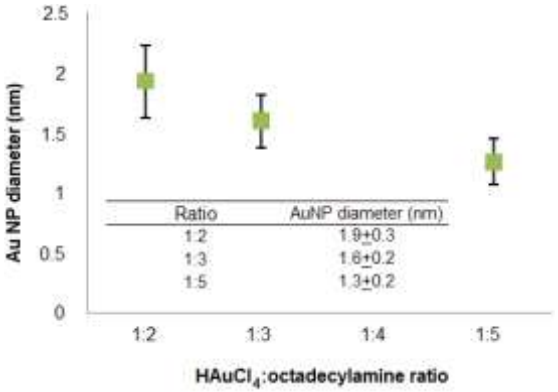


Figure S2: Effect of $HAuCl_4$:ligand molar ratio on the resulting AuNP diameter.

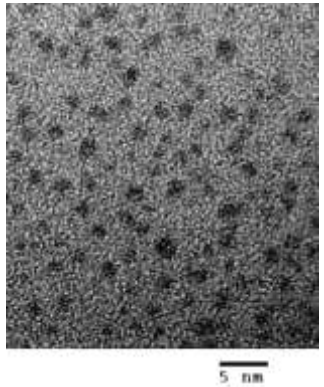


Figure S3: Representative TEM image of the gram-scale synthesis of AuNPs Reaction condition: octadecylamine used as ligand, at 29.5Hz for 90min, $HAuCl_4$:ligand of 1:5 ratio

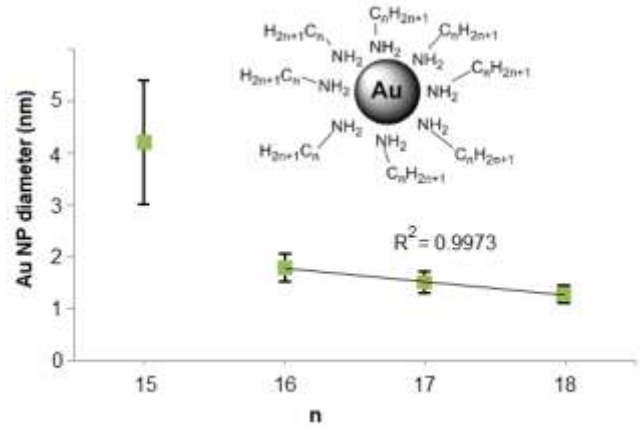


Figure S4: Dependence of the resulting Au NP diameter on the chain length of the amine ligand when long chain alkyl amines CnH2n+1NH2 are used (n=15 to 18). A linear trend is observed between n=16-18. Reaction conditions: 5:1 ligand:HAuCl4 ratio milled at 30 Hz for 90 minutes.

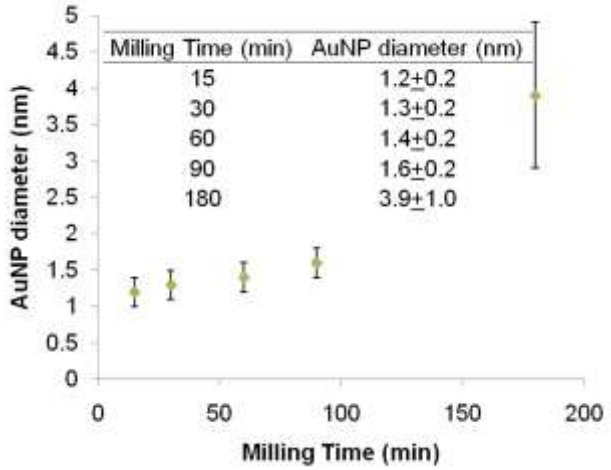
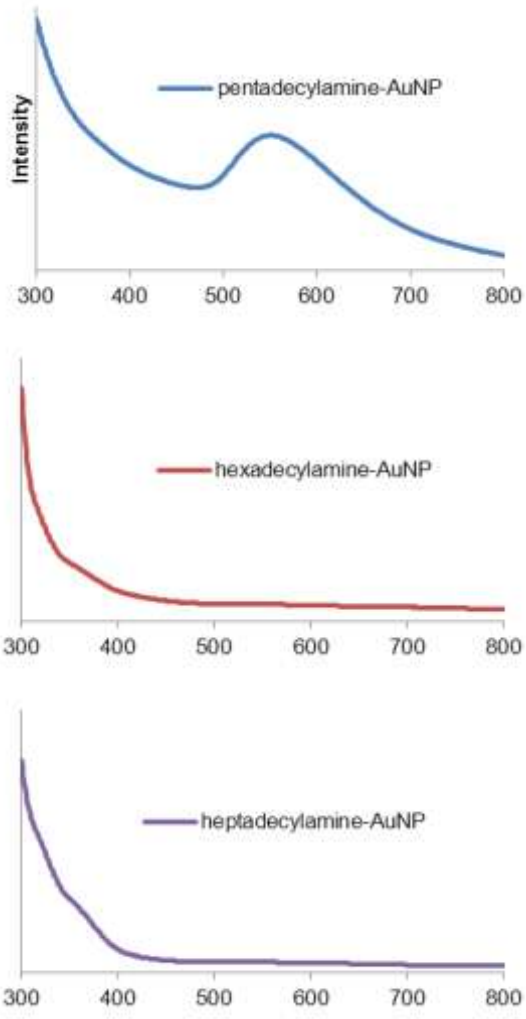


Figure S5: Effect of milling time on AuNP diameter. Reaction conditions: 5:1 moles octadecylamine:HAuCl4 milled at 29.5Hz

3. UV-Vis Spectroscopy Data



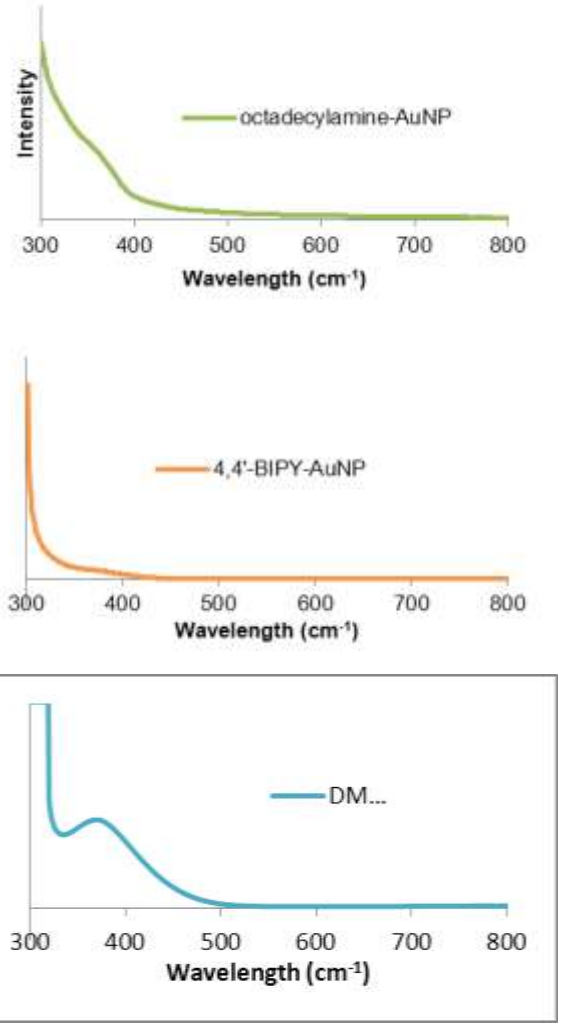


Figure S6: UV/Visible spectra of suspended AuNPs synthesized using different stabilizing ligands.

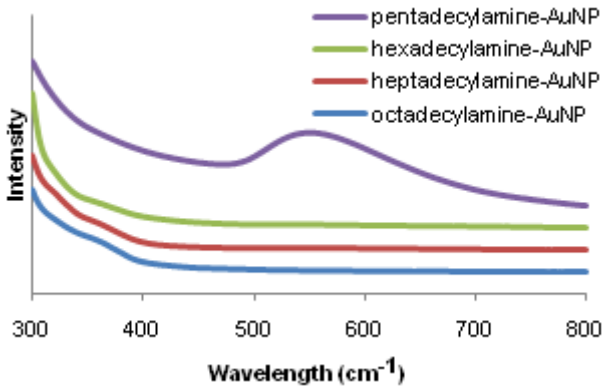


Figure S7: Direct comparison of UV/Visible spectra of suspended AuNPs synthesized using different alkyl amine stabilizing ligands.

4. XPS Data
(A survey of the regions of Ni and Cr indicated no presence of these metals in the sample)

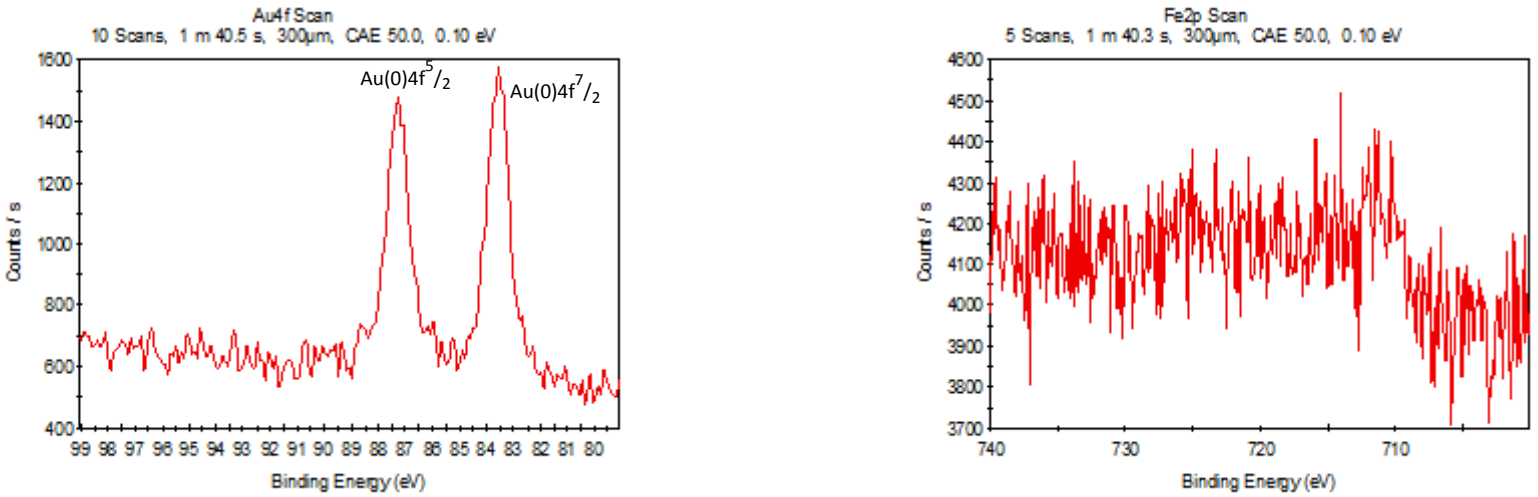


Figure S8: XPS spectra of the Au4f (left) and Fe2p (right) regions for pentadecylamine -AuNP:

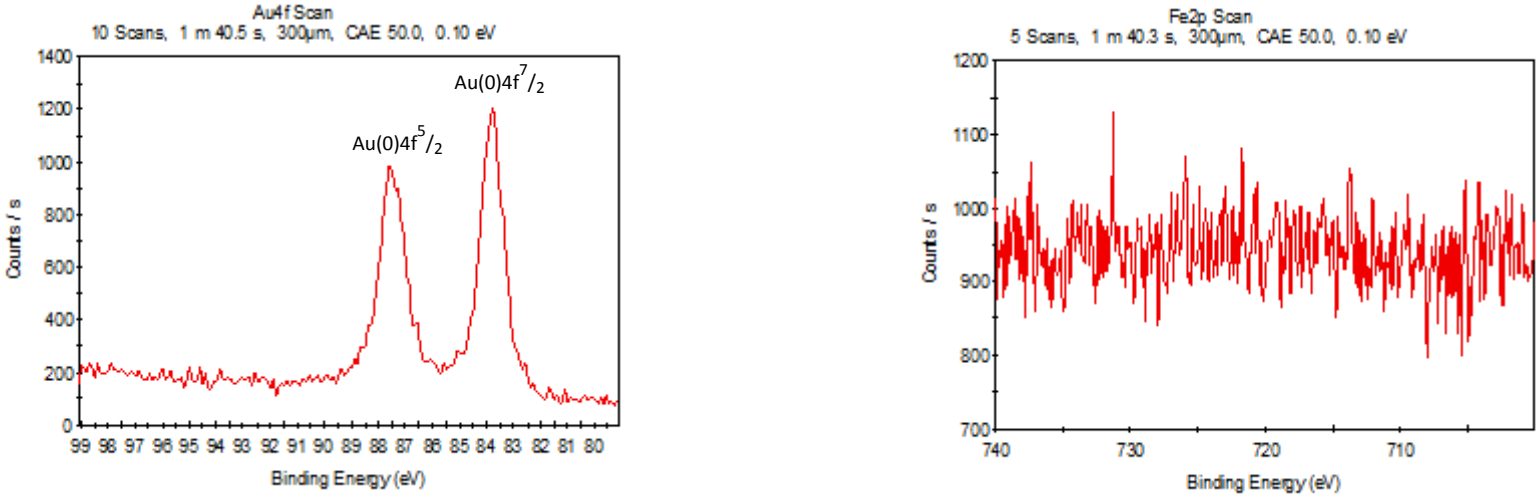
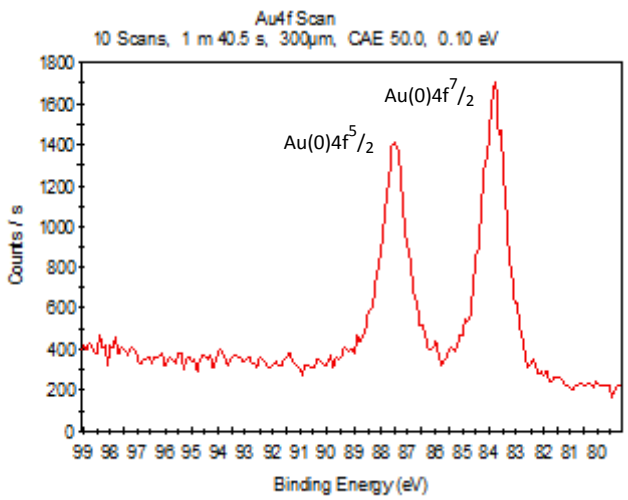


Figure S9: XPS spectra of the Au4f (left) and Fe2p (right) regions for hexadecylamine -AuNP:



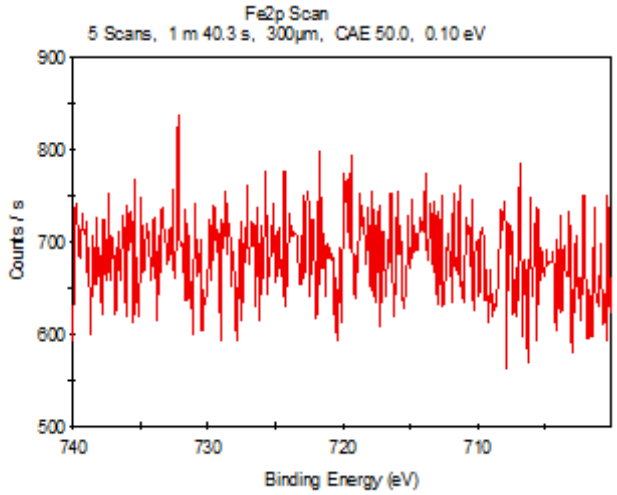
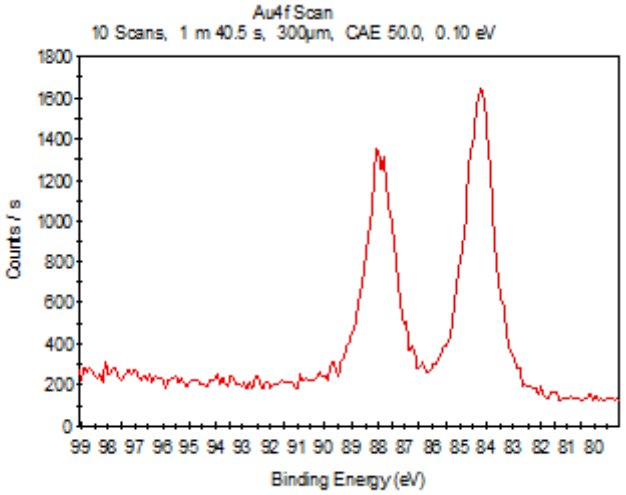


Figure S10: XPS spectra of the Au4f (left) and Fe2p (right) regions for heptadecylamine–AuNP



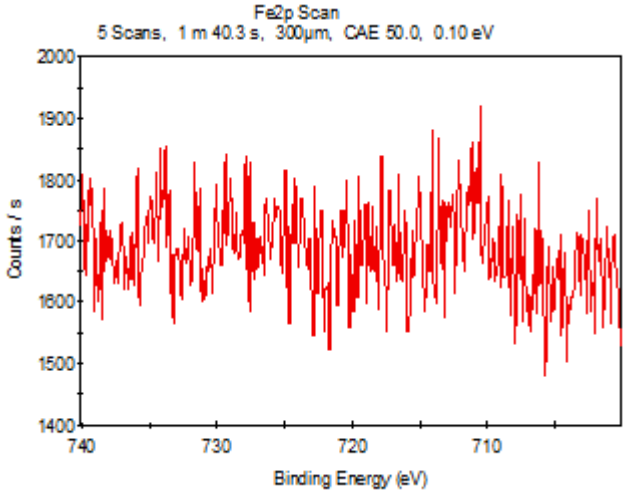


Figure S11: XPS spectra of the Au4f (left) and Fe2p (right) regions for octadecylamine -AuNP:

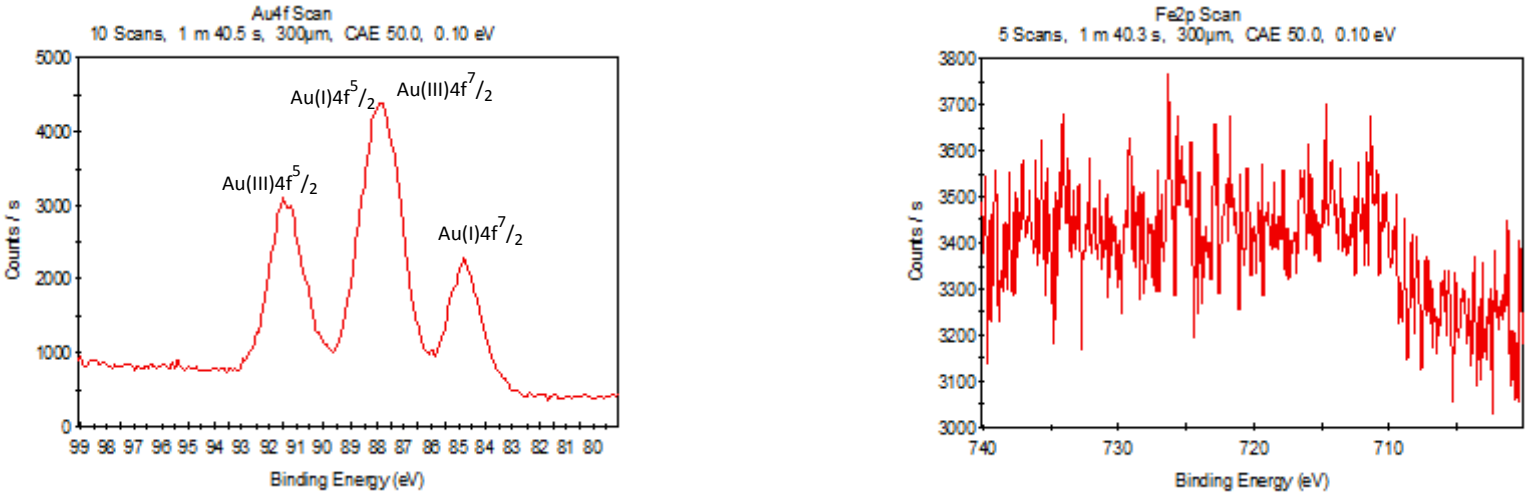


Figure S12: XPS spectra of the Au4f (left) and Fe2p (right) regions for DMAP –AuNP:

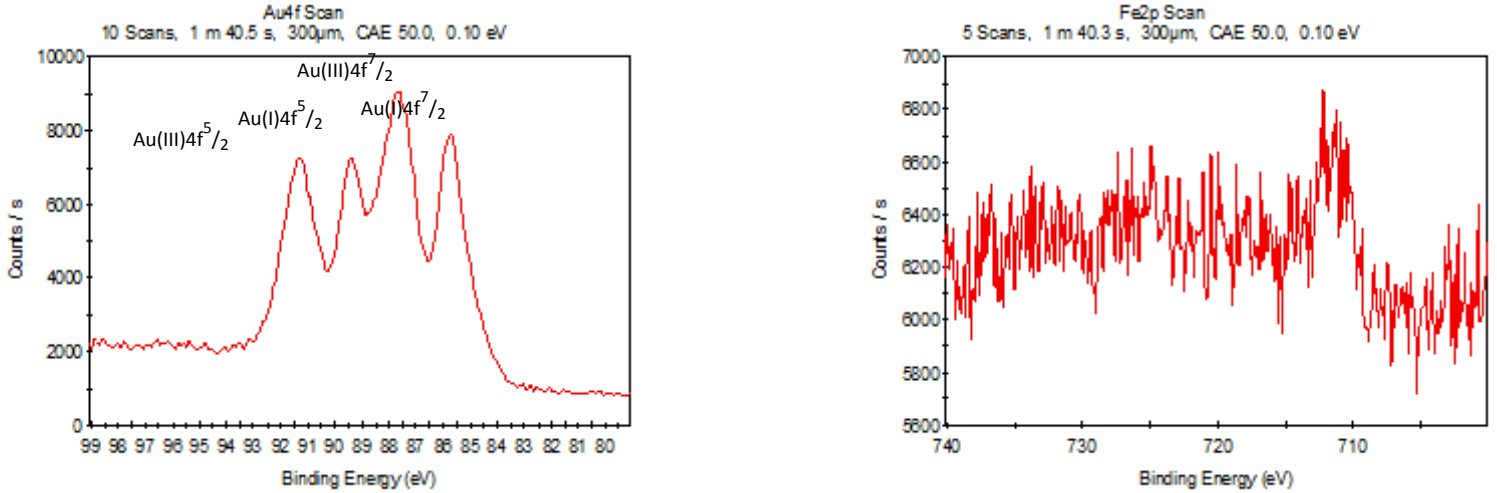
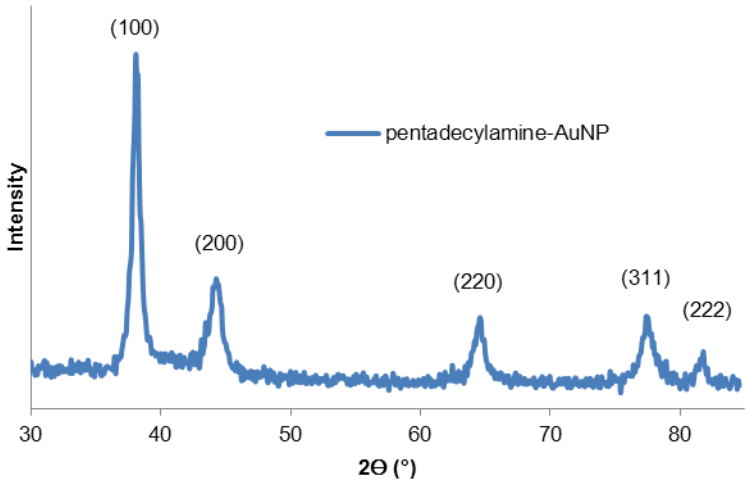
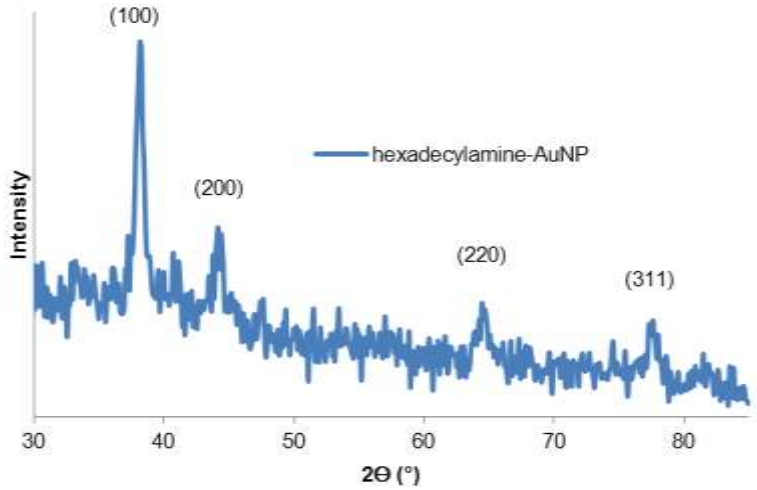


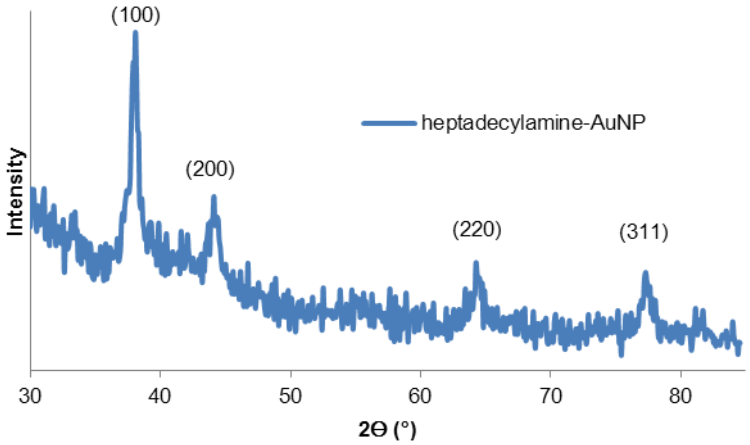
Figure S13: XPS spectra of the Au4f (left) and Fe2p (right) regions for 4,4`-BIPY-AuNP:

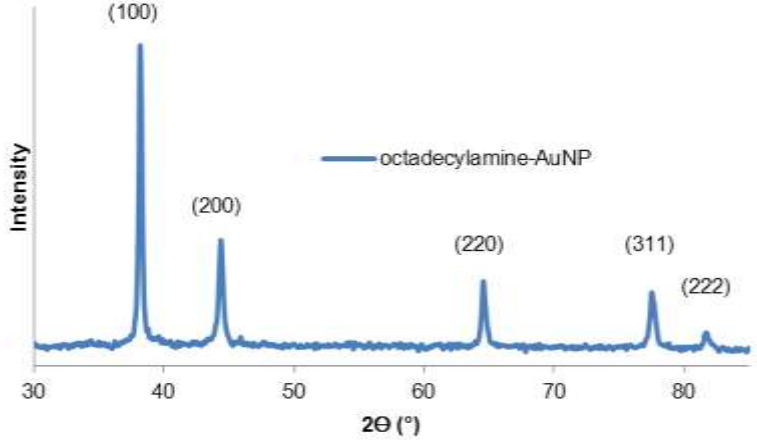
(using http://srdata.nist.gov/xps/Default.aspx to assign peaks)

5. Powder XRD Data









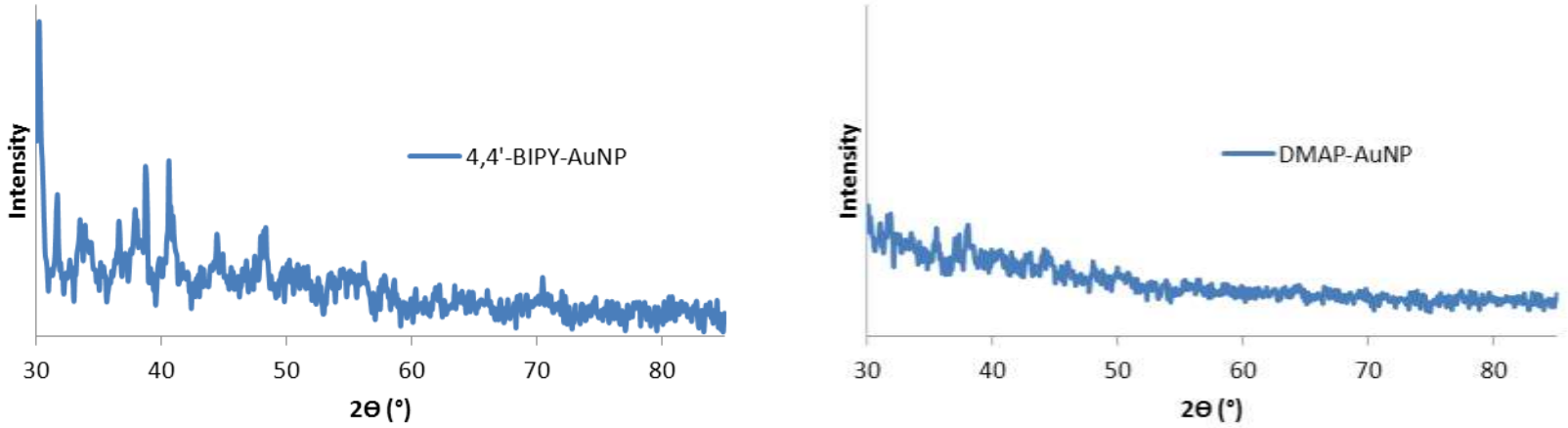


Figure S14: XRD patterns for AuNPs stabilized by a variety of ligands.

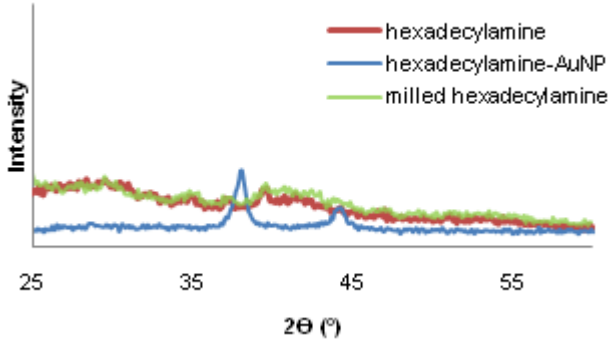


Figure S15: Comparison of powder XRD of hexadecylamine and hexadecylamine stabilized AuNPs. AuNPs synthesized by milling with 5 mol excess of ligand for 90 min at 29.5Hz.

6. Maldi-TOF MS

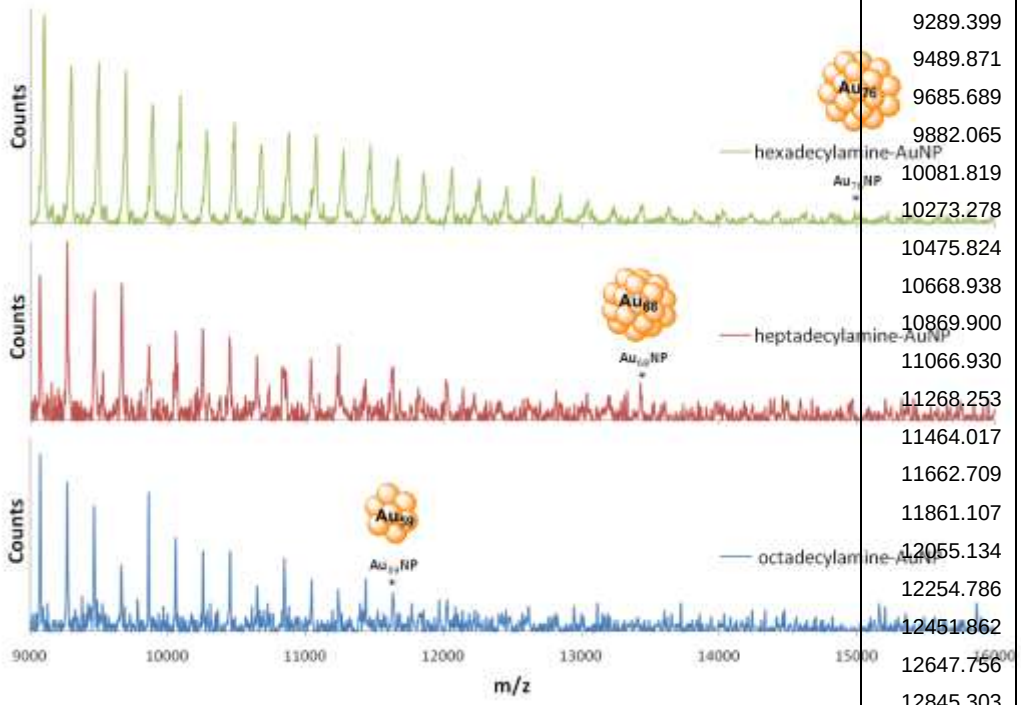


Figure S16: MALDI-TOF MS spectra for hexa-, hepta-, and octadecylamine stabilized AuNPs and the corresponding list of m/z peaks

C16 m/z	C17 m/z	C18 m/z
9093.234	9064.846	9065.421
9289.399	9262.412	9262.597
9489.871	9460.131	9458.478
9685.689	9658.168	9655.513
9882.065	9855.499	9854.068
10081.819	10050.983	10050.245
10273.278	10246.990	10249.222
10475.824	10443.481	10445.881
10668.938	10638.626	10641.809
10869.900	10837.926	10839.412
11066.930	11030.571	11038.214
11268.253	11235.200	11231.218
11464.017	11428.016	11430.241
11662.709	11628.193	11627.572
11861.107	11813.411	
12055.134	12011.295	
12254.786	12217.394	
12451.862	12407.157	
12647.756		
12845.303	12811.148	
13042.731	13037.657	
13232.598		
13425.392	13425.411	
13628.931		
13816.879		
14021.381		
14231.221		
14427.154		
14626.278		
14802.475		
15022.081		

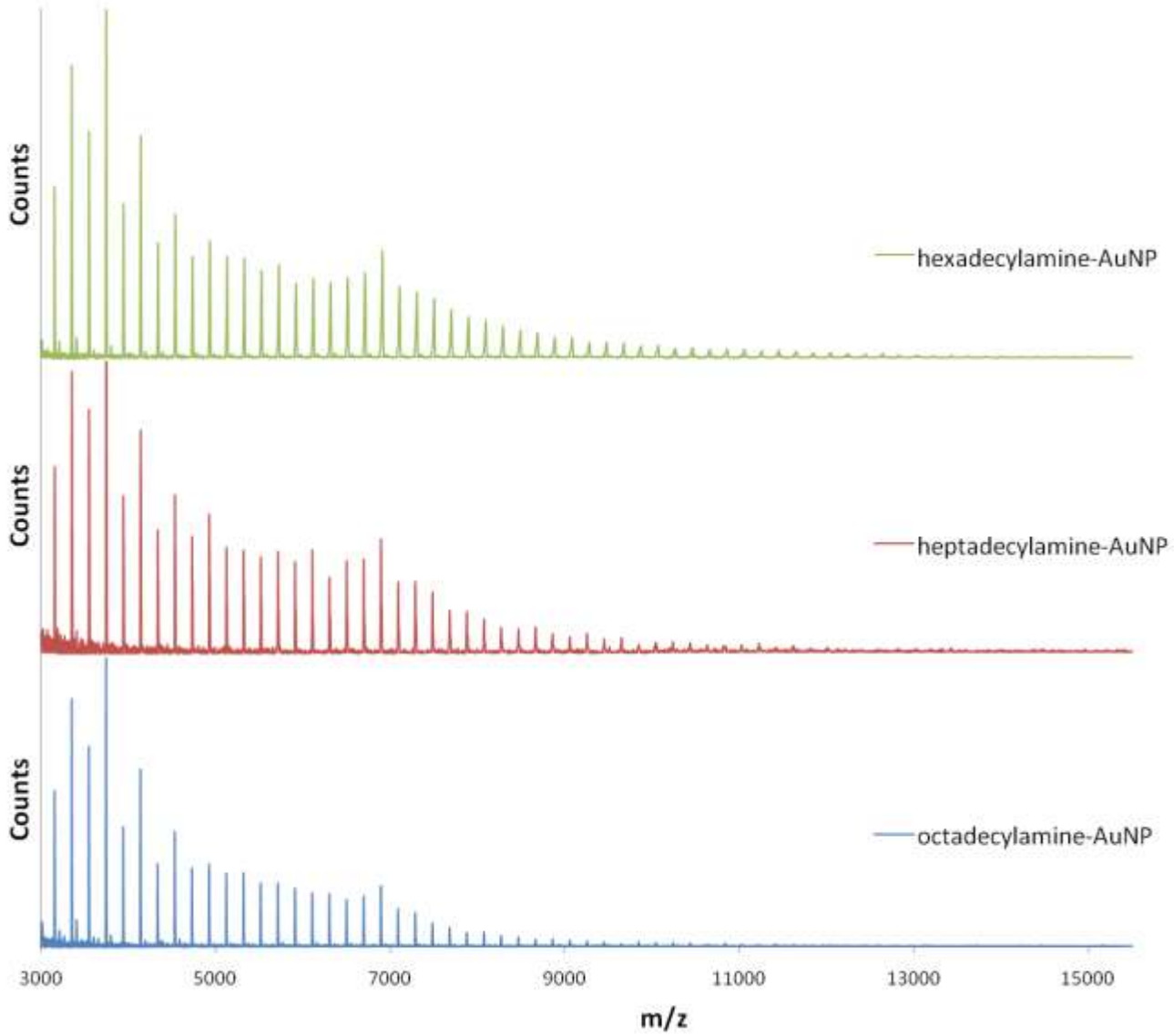


Figure S16: Expanded window of MALDI-TOF MS spectra for hexa-, hepta-, and octadecylamine stabilized AuNPs and the corresponding list of m/z peaks