Supporting Information

Multi-technique Characterization of Self-assembled Carboxylic Acid Terminated Alkanethiol Monolayers on Nanoparticle and Flat Gold Surfaces

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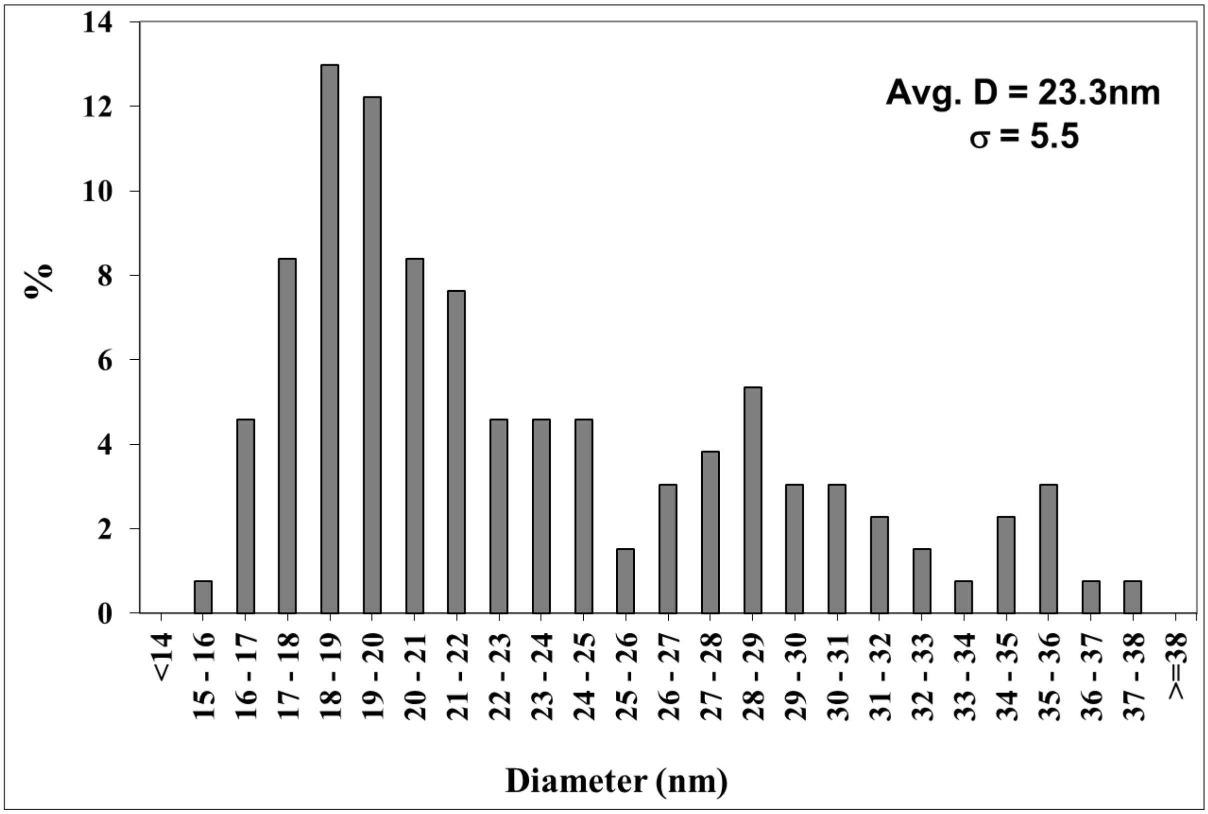

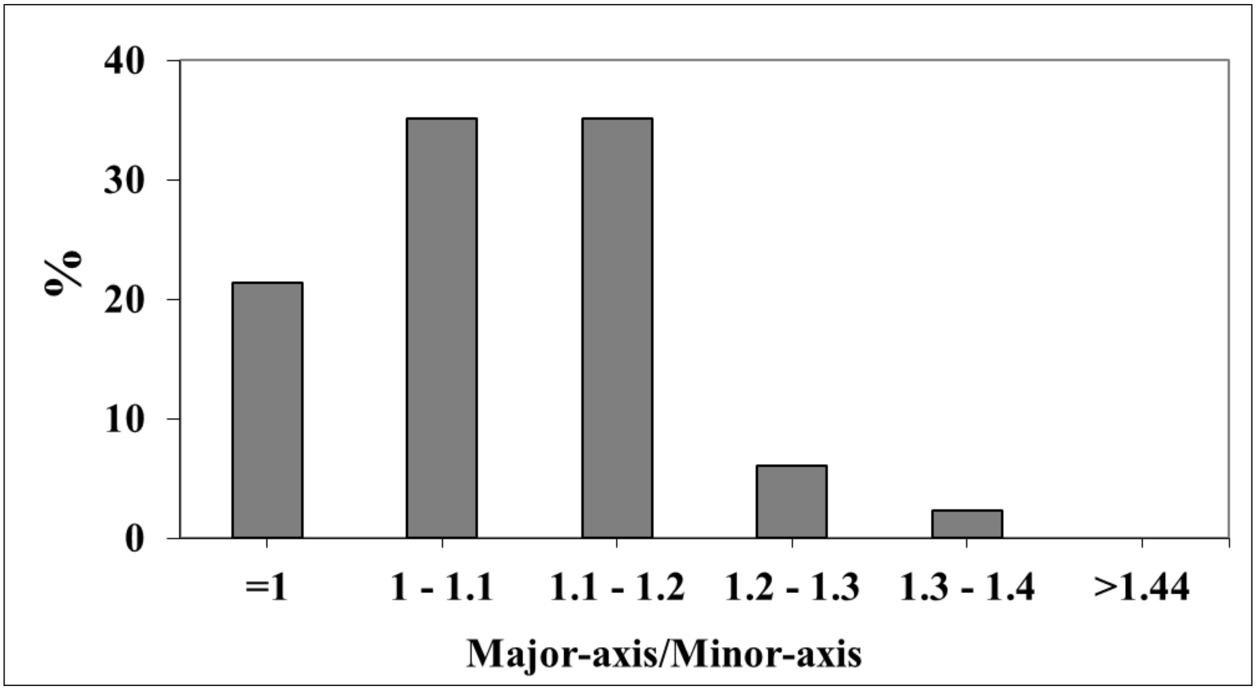

Figure S1. ImageJ analysis of the size distribution and circularity (defined as major axis/minor axis ratio) for the 25 AuNPs

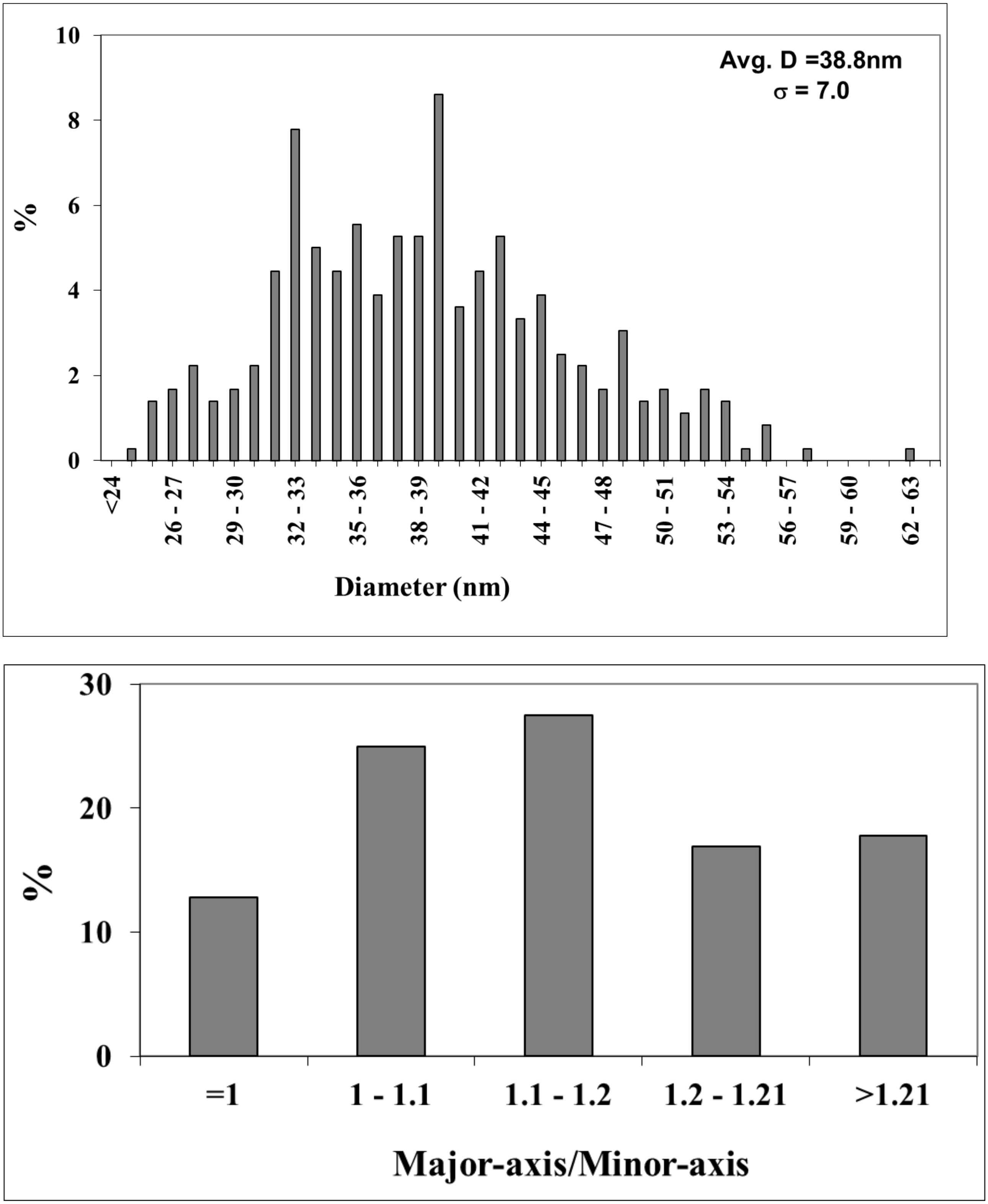

Figure S2. ImageJ analysis of the size distribution and circularity (defined as major axis/minor axis ratio) for 40nm AuNPs

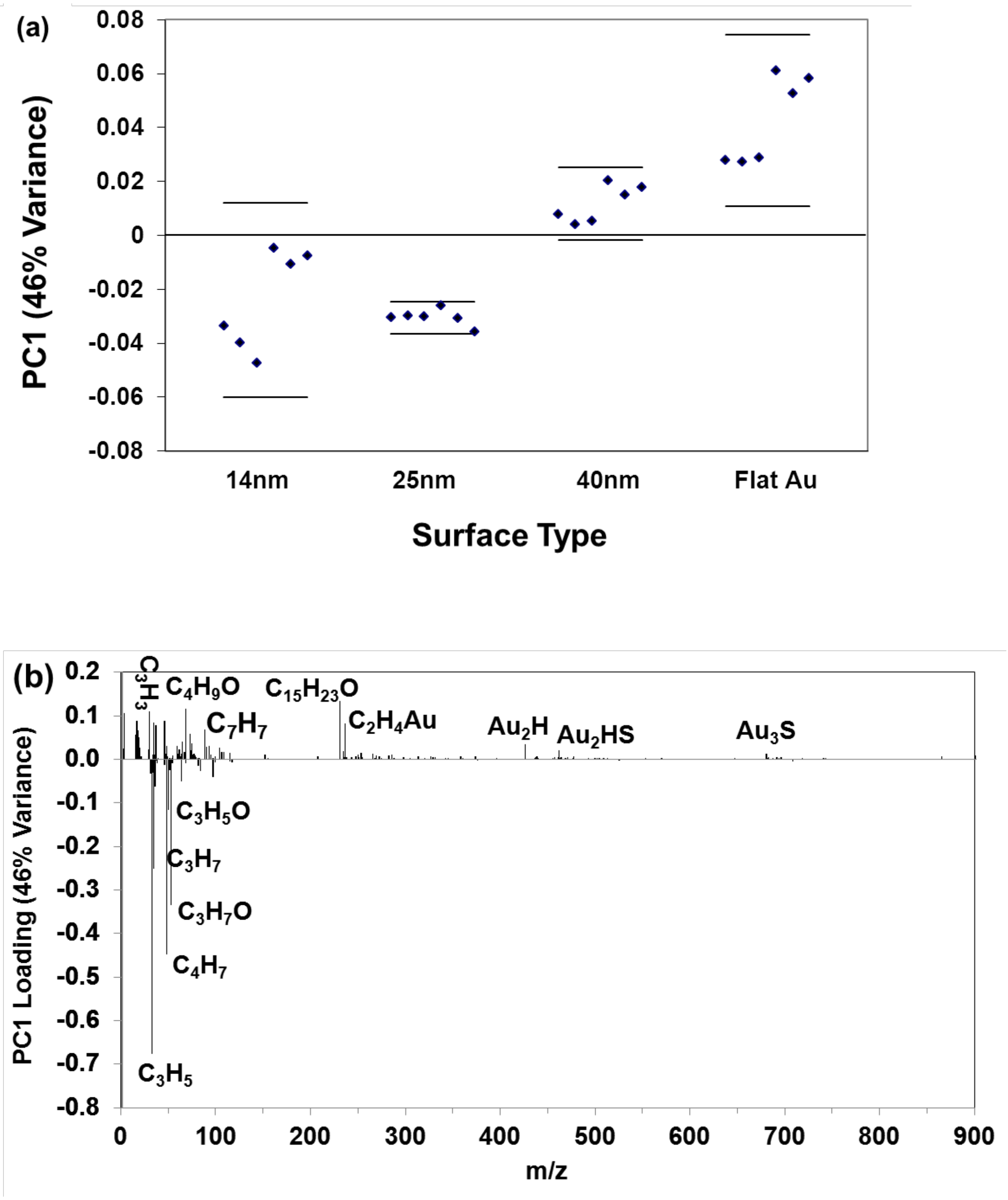

Figure S3. PC1 (a) scores with 95% confidence limits and (b) loadings for C16 COOH-SAMs on 14, 25 and 40nm AuNP and flat Au surfaces based on positive ion fragments from ToF-SIMS.

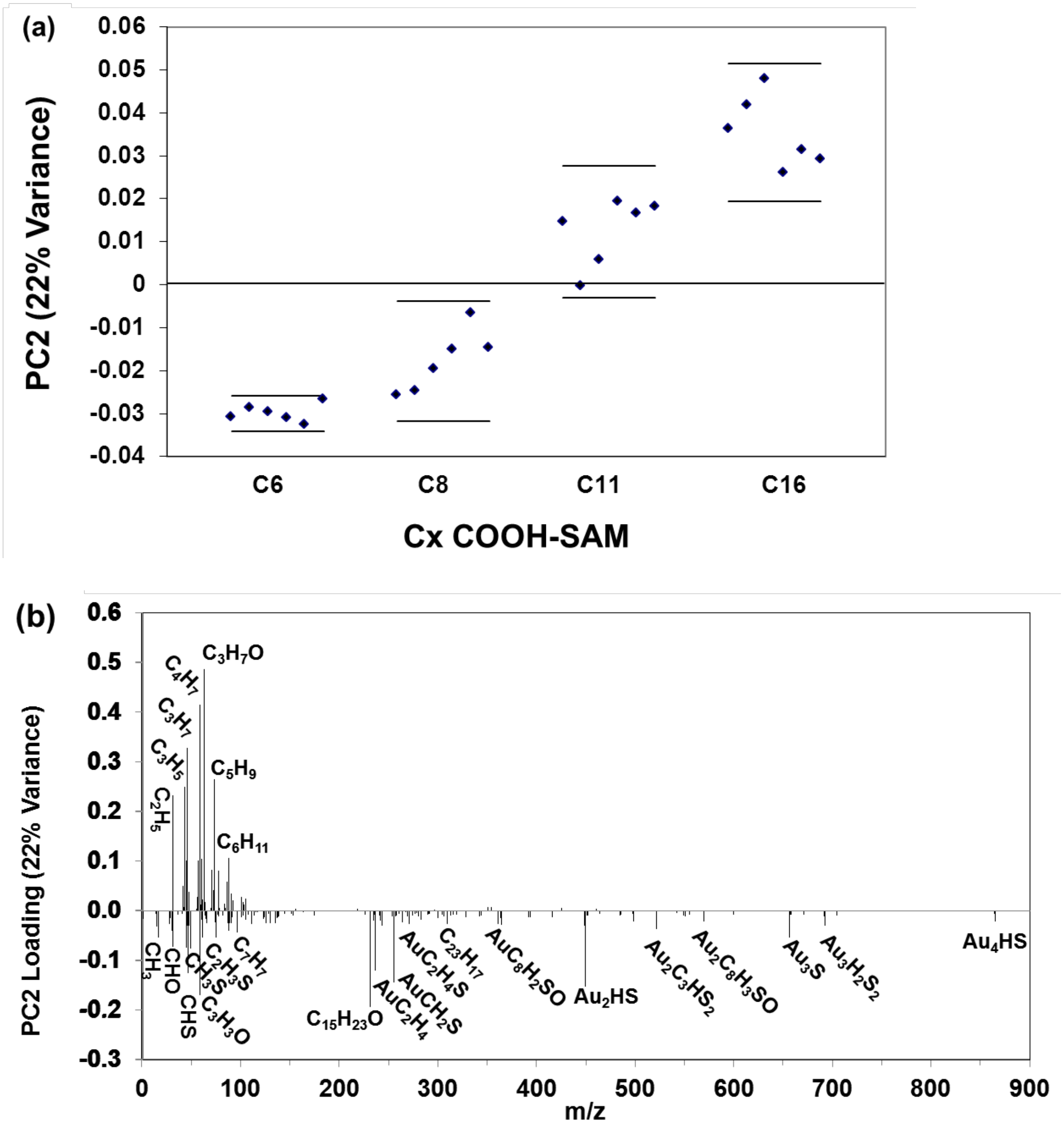

Figure S4. PC2 (a) scores with 95% confidence limits and (b) loadings for 14nm AuNPs functionalized with C6, C8, C11 and C16 COOH-SAMs based on positive ion fragments from ToF-SIMS.

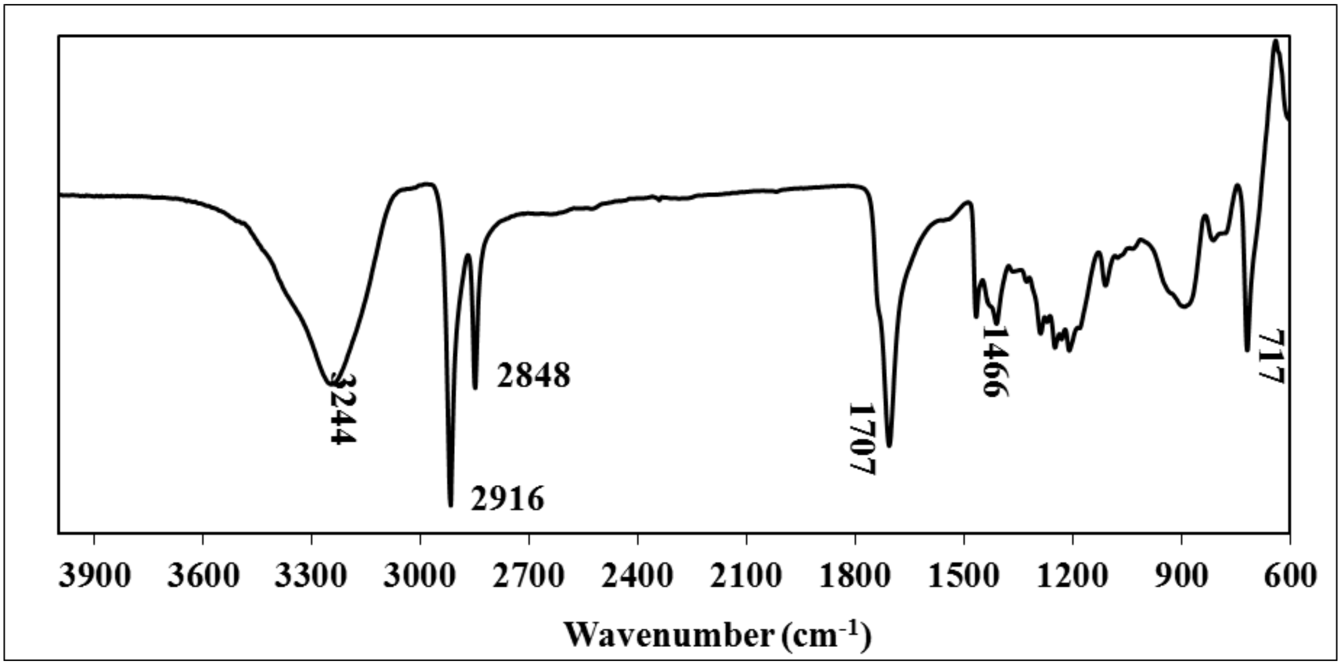

Figure S5. FTIR-ATR spectrum of a C16 COOH-SAM on 14nm AuNPs deposited onto a clean Si substrate.

UV/VIS Spectroscopy Analysis

Solution stability of AuNPs was analyzed using UV/VIS spectroscopy. Table S1 shows the values for the λ_{max}, FWHM and integrated areas for the main absorbance peak for all AuNP samples. The UV/VIS spectra were analyzed using the XPSPEAK data analysis program. The λ_{max} represents the surface plasmon resonant wavelength that gives the highest absorbance of light by the AuNPs. The λ_{max} red-shifted as the size of the citrate-AuNPs increased. The SAM functionalized AuNPs had red-shifted λ_{max} compared with the corresponding citrate-AuNPs. The C6 COOH-SAM functionalized AuNPs were observed to be the least stable, based on their large red-shift and the bluish color of their solutions. There was some solution aggregation observed for these AuNPs. For the same amount of starting $HAuCl_4$ reagent, a lower concentration of the larger AuNP is produced since they consume more Au atoms per nanoparticle. Also, the functionalization process further dilutes the AuNP concentration. These could create inconsistencies in the measured absorbance since variations in concentration of samples was not accounted for the values reported in Table S1. As the size of AuNPs increased the integrated area under the main peak of citrate-AuNPs also increased. This could be a net result of many factors including an increase in the size, polydispersity of size and shape of the AuNPs. Some aggregation was observed for the C16 COOH-SAM on 40nm AuNPs, as indicated by the peak appearing near 892nm λ_{max}.

Table S1. UV/VIS analysis of COOH-SAM on AuNPs. Average values are reported with standard deviations in parentheses.

Average Diameter (nm)	Surface Ligand: citrate ions or COOH SAM with C6, C8, C11, C16 chain lengths	λ_{max} ,nm (std. dev.)	FWHM	Area under the main peak
~14	Citrate	518.8 (0.2)	68.1 (0.7)	38.3 (0.0)
	C6	544.2 (0.3)	96.8 (1.0)	43.5 (0.4)
	C8	528.7 (0.1)	80.5 (0.5)	36.3 (0.1)
	C11	532.2 (0.1)	85.8 (0.1)	38.2 (0.1)
	C16	525.0 (0.1)	83.5 (0.2)	38.6 (0.1)
~25	Citrate	535.0 (0.3)	82.8 (0.7)	60.3 (0.4)
	C16	543.8 (0.3)	92.0 (0.7)	56.8 (0.4)
~40	Citrate	540.6 (0.1)	83.8 (0.2)	64.8 (0.2)
	C16	546.9 (0.1)	90.0 (0.4)	47.2 (0.4)
	C16 - aggregate	891.8 (3.3)	140.0 (8.5)	3.2 (0.5)