Electronic Supplementary Information: Tuning the magnetism of gold nanoparticles by changing the thiol coating

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Experimental

Chemicals

Gold(III) chloride trihydrate (>99.5 %), tetraoctylammonium bromide (TOAB, 98 %), sodium borohydride (98.5 %), acetonitrile (HPLC grade), chloroform (HPLC grade), and dichloromethane (HPLC grade) were obtained from Sigma-Aldrich Canada. All thiols (heptanethiol, nonanethiol, undecanethiol, hexadecanethiol, 11-mercapto-1-undecanol, and 11-mercapto-1-undecanoic acid) were purchased from Sigma-Aldrich Canada (reagent grade). Toluene (99.5 %) was obtained from Caledon Laboratory Chemicals. Anhydrous ethanol was obtained from Commercial Alcohols Canada. ACS reagent grade solvents were used from Sigma Aldrich for UV-vis spectroscopic experiments and TEM sample preparations. All chemicals were used as-received without further purification. Deionized water was made to a resistivity of 18.2 $\mathrm{M\Omega \cdot cm^{-1}}$.

Gold nanoparticle synthesis

Au NP Synthesis. A modified Brust-Schiffrin synthesis was used to prepare the gold nanoparticles.[18,19] In the case of alkanethiols heptanethiol, nonanethiol, undecanethiol and hexadecanethiol, 30 mL of a 3-mM aqueous solution of $\mathrm{HAuCl_4 \cdot 3\,H_2O}$ was added to 80 mL of a 50-mM solution of TOAB in toluene, and stirred until the aqueous phase appeared colorless. Then, 0.84 mmol of the desired alkanethiol was added to the organic phase and left to stir until the solution changed from red to colorless. Within 2 to 4 hours of thiol addition, a fresh aqueous solution of $\mathrm{NaBH_4}$ (0.4 M, 25 mL) was added drop-wise at a rate of 2-3 drops per second. The solution quickly turned dark brown and was left to stir in an open flask for 2-3 h. The organic phase was separated, concentrated to <10 mL, diluted with approximately 200 mL of anhydrous ethanol, and kept at 4 ° C overnight. The nanoparticles in each case would precipitate out of solution. Gold nanoparticles coated with heptanethiol, nonanethiol, undecanethiol and hexadecanethiol respectively are referred to as **7-H**, **9-H**, **11-H** and **16-H** emphasizing the carbon chain length and the identity of the terminal group.

For the mixed thiols, in the case of 11-mercapto-1-undecanol (its product referred to as **11-OH**), a total of 0.84 mmol of 11-mercapto-1-undecanol and 1-undecanethiol with mole ratio of 3:1 were added to the reaction mixture and stirred for 3 hours. Next, 25 mL of a freshly prepared 0.4 M aqueous solution of $\mathrm{NaBH_4}$ was added drop-wise to the reaction mixture which was then stirred for an additional 3 hours. The particles were collected from the organic layer in the same manner as for alkanethiols. As for 11-mercapto-1-undecanoic acid (giving rise to **10-COOH** nanoparticles), essentially the same preparation was used; in that synthesis, an initial mole ratio of 1:9 11-mercapto-1-undecanol to 1-dodecanethiol was used[18,19].

Purification and Composition Analysis. In order to remove residual thiol and TOAB, the Au NPs were repeatedly dispersed into acetonitrile using a vortexer and then centrifuged for 30 minutes, with the supernatant removed between cycles. This process was repeated until no evidence of unbound thiol remained upon ^{1}H NMR analysis of the nanoparticles. ^{1}H-NMR was performed in $\mathrm{CDCl_3}$ on a JEOL JNM-GSX 270 MHz spectrometer[18,19]. Purity from unbound alkanethiol was determined by the absence of a peak for the α-hydrogen, and the presence of peaks corresponding to the methylene hydrogens and the terminal methyl hydrogens; as outlined in Fisher *et al.* the result were of high purity.[18] For both cases involving mixed thiols, the final thiol composition in the product was confirmed using NMR analysis of the decomposition product when treated by iodine, as outlined by Fisher *et al.*.[18] The result were 70 % 11-mercapto-1-undecanol with 30 % undecanethiol for **11-OH**, and 6 %11-mercapto-1-undecanoic acid with 94 % dodecanethiol for **10-COOH**

Characterization

UV-Vis spectroscopy. UV-vis spectra were measured for the NP suspensions in a 5-mm pathlength quartz cuvette with a Cary 500 spectrophotometer. The solvent of choice was chloroform, except for **11-OH**, for which methanol was used.

Transmission electron microscopy. Formvar and carbon-coated 200 mesh Cu transmission electron microscopy (TEM) grids were obtained from Ted Pella. Samples for TEM were prepared by letting a droplet of dissolved nanoparticles dry on the grid in air.

Bright-field TEM images were acquired with a FEI Tecani 20 microscope operating at 200 kV. Images were analysed using ImageJ.[49,50]

Ultraviolet photoelectron spectroscopy. For ultraviolet photoelectron spectroscopy (UPS), solutions of the nanoparticles were drop-cast onto a clean 1×1 cm^2 Si(100) wafer and left to dry in air. A Kratos AXIS Ultra was used for the measurement at the University of Alberta's NanoFab research facility. It utilizes a He(I) source with 21.21 eV photon energy and has a spot size of less than 5 mm. Step size during measurement was 0.05 eV, and calibrated against pure gold's Fermi level. No charge neutralization was applied. The UPS data were analyzed using *Casa XPS*.[51] Various ways to pin-point the edges exist. The secondary edge is defined as the binding energy at half the peak height. The Fermi edge is set to the inflection point, approximated by fitting the S-shaped Fermi edge with three straight lines, and taking the mid-way point between the two intercepts formed by the first and second, and second and third lines, as the inflection point (Figure S3).

Magnetometry. Superconducting quantum interference device (SQUID) magnetometry measurements were carried out using a Quantum Design MPMS XL-7S magnetic property measurement system. Each nanoparticle powder sample was loaded in a size 4 Snap-fit gelatin capsule (Ted Pella, Inc.; product number 130-20), sealed with minimal amount of 0.25-inch Kapton tape, and inserted in a clear and diamagnetic plastic straw.

For both zero-field-cooled (ZFC) and field-cooled (FC; $\mu_0 H = 10$ mT) measurements, the samples were first cooled to 1.9 K in the absence (FC) or presence (ZFC) of a 10 mT field; the magnetization was measured as the sample was warmed to 300 K under 10 mT. ZFC measurements always preceded FC. Magnetization reversal loops were measured at temperatures of 300 K and 1.9 K, with applied field up to 1 T, or the minimum needed for saturation.

In order to correct for the diamagnetic response of large number of inner-shell electrons of gold as well of contribution from holder, a $M(H)$ H loop at high (5 T) field was run; from this, a straight line is fitted through the linear high-field portion of this loop. This straight line provides the diamagnetic susceptibility (Table S3) of the holder and sample, and was subtracted from the $M(H)$ hysteresis loops shown.

Tables

Sample	$\mu_0 H_c^{300K}$ (mT)	M_r^{300K} (emu g^{-1})	$\mu_0 H_c^{1.9K}$ (mT)	$M_r^{1.9K}$ (emu g^{-1})
7-H	0.0068	0.00068	0.0016	18.2
9-H	0.0072	0.00083	0.0019	13.8
11-H	0.0074	0.0013	0.0021	13.8
16-H	0.0075	0.0014	0.0024	15.1
11-OH	0.0063	0.0021	0.0048	12.2
10-COOH	0.0094	0.0035	0.0060	19.1

Table S1 More properties from SQUID measurement of applied-field dependence: coercive field $\mu_0 H_c$ and remanent magnetization M_r at 300 and 1.9 K

Size (nm)	Coating	M_s		T (K)	Reference
–	polyallyl amine hydrochloride	22	μ_B NP^{-1}	1.8	Yamamoto & Hori[31]
1.4	dodecanethiol	0.4	emu g^{-1}	300	Crespo *et al.*[29]
1.4	dodecanethiol	1	emu g^{-1}	5	Crespo *et al.*[29]
1.9	dodecanethiol	5	emu g^{-1}	300	Garitaonandia *et al.*[32]
2.5	polyvinylpyrrolidone	1.7	emu g^{-1}	300	Hori *et al.*[5]
2.5	polyvinylpyrrolidone	1.7	emu g^{-1}	300	Hori *et al.*[5]
2.5	dodecanethiol	0.16	emu g^{-1}	300	Maitra *et al.*[33]
5	dodecanethiol	1×10^{-4}	emu g^{-1}	300	Dutta *et al.*[30]
5	dodecanethiol	3×10^{-3}	emu g^{-1}	5	Dutta *et al.*[30]
1.9	polyallyl amine hydrochloride	0.02	emu g^{-1}	2.6	Yamamoto *et al.*[34]
2.5	polyallyl amine hydrochloride	1.35	emu g^{-1}	1.8	Hori *et al.*[14]
2.5	dodecanethiol	0.1	emu g^{-1}	1.8	Hori *et al.*[14]
2.5	polyvinylpyrrolidone	1.7	emu g^{-1}	1.8	Hori *et al.*[14]
2.0	dodecanthiol	0.09	emu g^{-1}	300	Guerrero *et al.*[36]
2.0	dodecanthiol	0.05	emu g^{-1}	5	Guerrero *et al.*[36]
1.8	SRmaltose	0.017	emu g^{-1}	300	Crespo *et al.*[37]
2	SRlactose	0.004	emu g^{-1}	300	Crespo *et al.*[37]
3.2	dodecanethiol / polymer film	0.05	emu g^{-1}	300	de la Venta *et al.*[38]

Table S2 Compilation of saturation magnetizations reported for Au NPs

Sample	300 K (-10^{-8}emu g^{-1}Oe^{-1})	1.9 K (-10^{-8}emu g^{-1}Oe^{-1})
7-H	1.805	1.296
9-H	1.555	1.319
11-H	1.658	1.493
16-H	1.774	1.513
11-OH	1.782	1.543
10-COOH	1.669	1.482

Table S3 Diamagnetic correction for M vs H data, consisting of slopes of the hysteresis loop at high fields (5-7 T). These are already subtracted from M vs H data shown previously

Figures

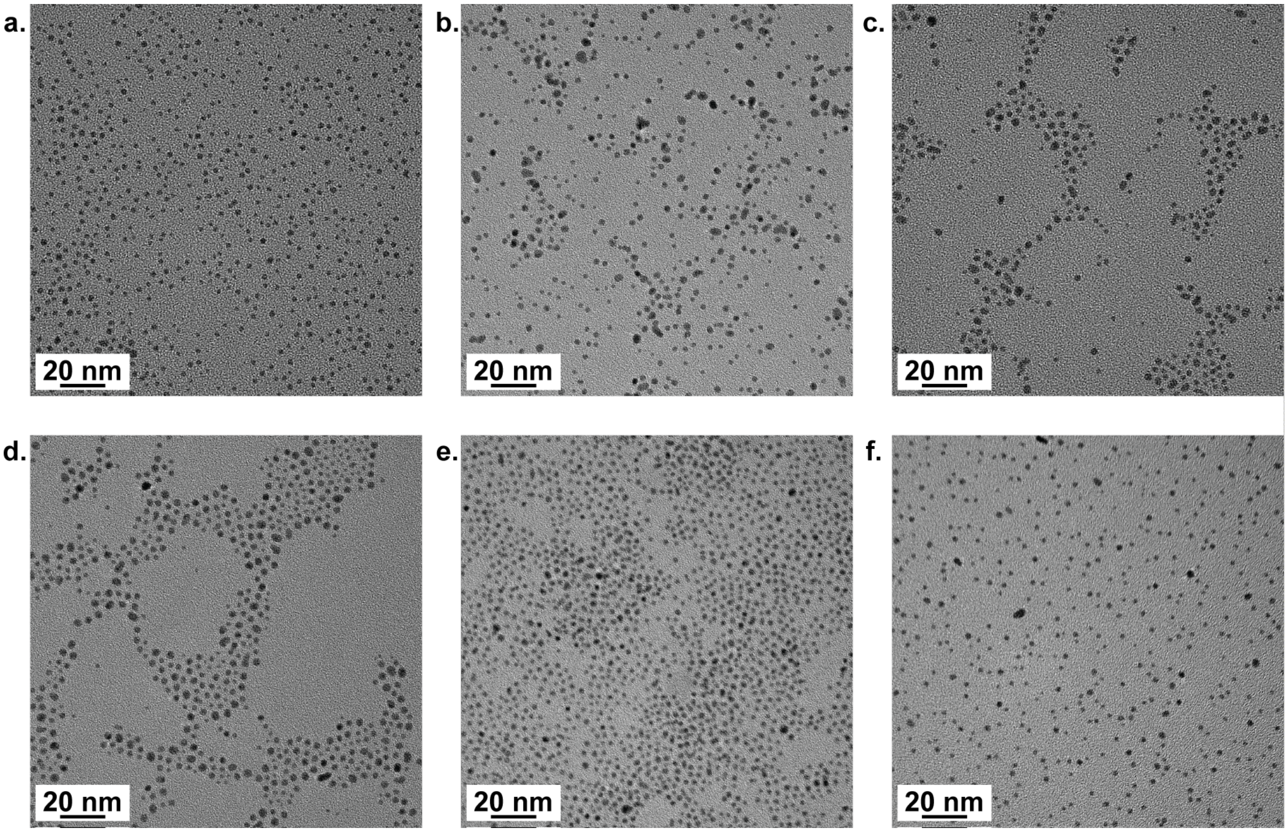

Fig. S1 Representative TEM image for each nanoparticle sample tested. (a) **7-H**, (b) **9-H**, (c) **11-H**, (d) **16-H**, (e) **11-OH**, (f) **10-COOH**.

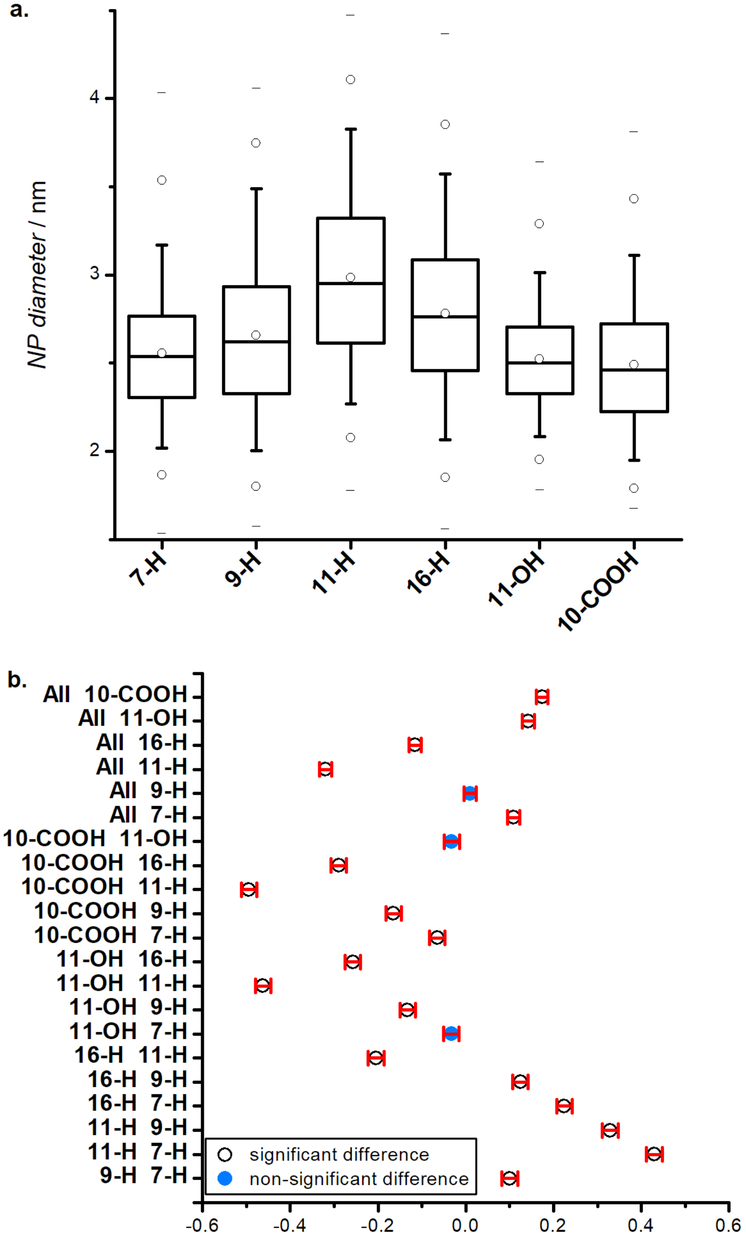

Fig. S2 a. In the boxplot, the distribution of diameter for each type of NP is plotted around its median; for the box, the first quartile (its lower edge) is the middle number between the smallest number and the median of the data set and the third quartile (upper edge) is the middle value between the median and the highest value of the data set. The outliers, represented in circles, when present tend to be larger NPs. One can see that all the nanoparticle samples have good normal distribution, with no skew. Outliers tend to be oversized particles. **b.** Multiple comparison simultaneously compares several means with each other, enabling us to determine if there is statistical significance between means, under a certain criteria. If they are, pair wise tests allow us to say with some confidence that a particular pair is different or not. For such a task, analysis of variance (ANOVA) was performed between all possible pairs of NPs to test for any significant differences in the diameter, and since the results have p value close to zero, Tukey's test is employed. Apart from two pairs: **11-OH** and **10-COOH**, **11-OH** and **7-H**, for which within 95 % confidence interval one can conclude they have the same average size, no two sets of NP have the same size distribution.

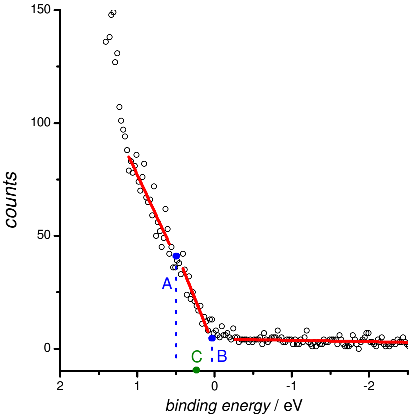

Fig. S3 Locating the Fermi edge for UPS data. The *S*-shaped Fermi edge is fitted with three separate straight lines, and the binding energy at half way between the two intercepts A and B these three lines make, is considered to be the binding energy at the Fermi edge (C).