Supporting Information

NMR Characterization of Ligand Binding and Exchange Dynamics in Triphenylphosphine Capped Gold Nanoparticles

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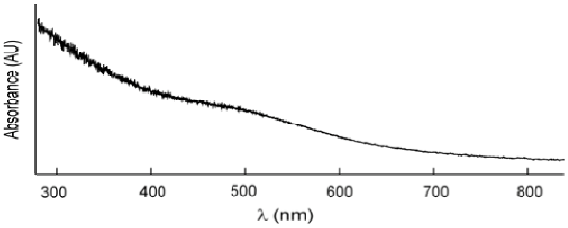
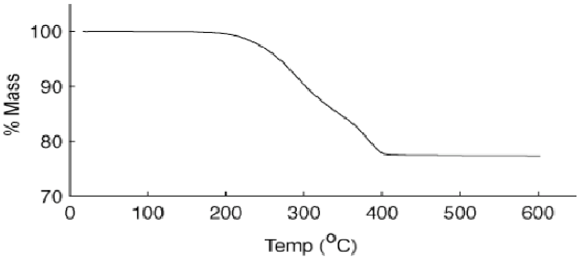
UV-Vis



S1. UV-Vis absorption spectrum of PPh_3 capped gold nanoparticles dissolved in CH_2Cl_2.

An ultraviolet-visible (UV-Vis) absorption spectrum was collected on a solution of PPh_3 capped 1.8 nm AuNPs dissolved in CH_2Cl_2 (0.5 mg/ml) using an Ocean Optics Instrument. A UV-Vis spectrum is shown in figure S1. The amplitude and position of the plasmon band can be used as a guideline to predict the nanoparticle core size. UV-Vis absorption spectrum shown in figure S1 does not show any significant plasmon resonance around 520 nm, which indicates that the majority of the sampled nanoparticles are < 2.0 nm in diameter.[1] This result is consistent with statistical data derived from TEM images of the nanoparticles (Figure 1).

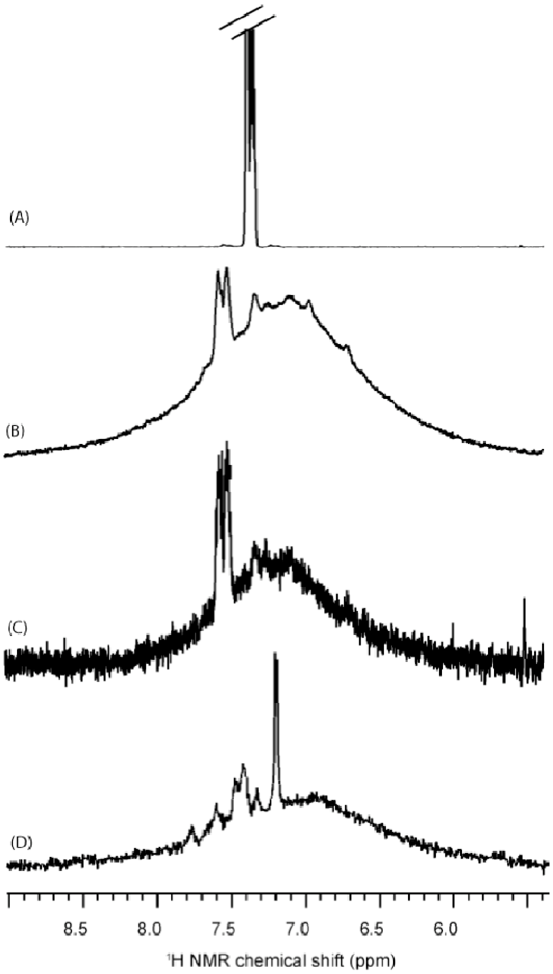
TGA



S2. TGA analysis of PPh_3 capped 1.8 nm AuNPs. A loss of 23% mass occurred when the sample was heated > 400 °C.

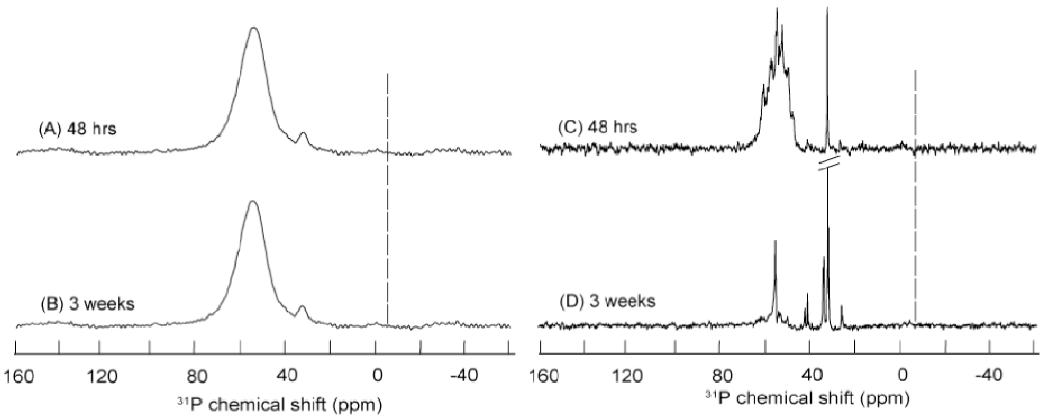
Thermal gravimetric analysis (TGA) of the nanoparticles was performed (SETARAM Instrument) to measure the mass associated with surface bound PPh_3 and gold core, respectively. The temperature was raised from room temperature to reach 600 °C at a rate of 10 °C/min under a helium atmosphere. At the end of the experiment, the remaining gold from the sample of nanoparticles was recovered from the alumina sample holder. The TGA data reported in figure S2 shows that the surface bound organic ligands contribute 23 % of the total mass of the nanoparticles. The loss in mass occurs before the temperature reaches 400 ^{o}C, beyond which no apparent loss is detected. This is consistent with 1.8 nm gold nanoparticles capped with an average of 24 PPh_3 ligands and 12 Cl^- ions as separately determined from elemental analysis.

^{1}H NMR line broadening in PPh_3 capped gold nanoparticles: ^{1}H solution NMR were acquired under different experimental conditions to understand NMR line broadening mechanisms in PPh_3 capped gold nanoparticles and the resulting data is shown in figure S3. Spectra collected for free ligand, concentrated nanoparticle solution, dilute nanoparticles solution and magic angle spinning (MAS) of solution rotating at 5 KHz are shown in a stacked plot. The first three spectra (A-C) were collected with a single pulse NMR experiment in a 500 MHz Varian instrument and the fourth spectrum (D) was collected with single pulse in a 400 MHz WB Varian NMR instrument under MAS conditions. The ^{1}H line around 7.1 ppm is associated with phenyl protons and under all conditions shows substantial broadening compared to the free PPh_3. This broadening is heterogeneous as shown by hole burning NMR experiment (figures 2 and 3) and attributed to different chemical shift environments on the nanoparticle surfaces.



S3. ^{1}H NMR of (A) free PPh_3 in CD_2Cl_2 solution; (B) high concentration (10 mg/ml) and (C) lower concentration (1 mg/ml) of PPh_3 capped AuNPs dissolved in CD_2Cl_2; and (D) MAS spectrum of PPh_3 capped AuNPs solution in CD_2Cl_2 (10 mg/ml) collected at 5 kHz MAS The resonance at 7.2 ppm is due to residual $CHCl_3$ used in the end of nanoparticles purification step. All ^{1}H data is plotted over the same ppm range (5.4 to 9 ppm)

The sharp resonances that overlapping the broad PPh_3 capped AuNPs ^1H resonances (B-D) are assigned to $Au(PPh_3)Cl$ at 7.5 ppm and residual chloroform at 7.2 ppm.

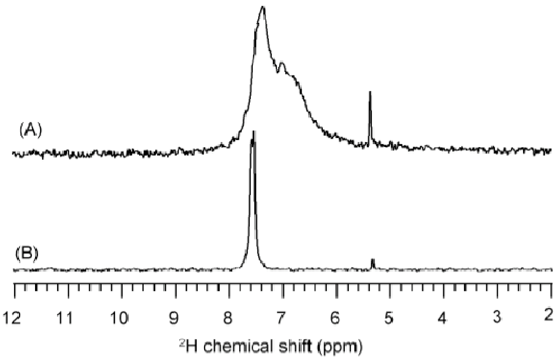


S4. ^{31}P solid-state MAS NMR collected on solids PPh_3 capped 1.8 nm AuNPs after storing at room temperature for (A) 48 hrs and (B) 3 weeks. ^{31}P solution NMR collected on solution sample dissolved in CD_2Cl_2 and stored at room temperature for (C) 48 hrs and (D) 3 weeks in the Teflon sleeved NMR tube. All samples were obtained from a same synthesis batch. Dashed lines at ~5 ppm is the chemical shift of free PPh_3.

Stability of PPh_3 capped gold nanoparticles assessed by ^{31}P NMR. The ^{31}P solid-state MAS and solution-state NMR of PPh_3 capped AuNPs in figure S4 is shown in an attempt to compare the stability of nanoparticles stored in solution or as dry powders for an extended period of time. It is clear from the ^{31}P NMR spectra that that nanoparticles in solution decompose over a short period of time, while PPh_3 capped AuNPs stored, as a dry powder is significantly more stable against decomposition.

Deuterium (^2H) solution NMR.

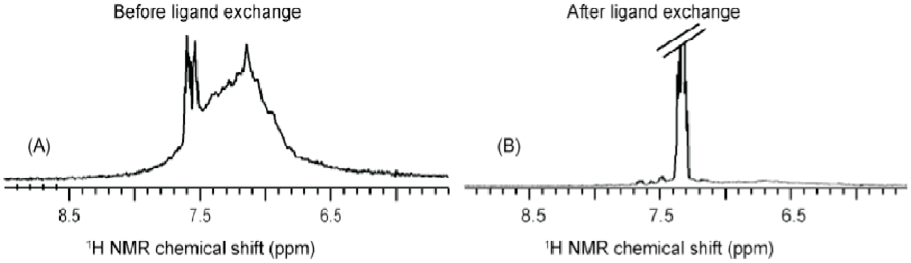
^2H NMR spectra were collected on PPh_3 capped AuNPs exchanged with d_{15}-$Au(PPh_3)Cl$. Ligand exchange was performed by addition of d_{15}-$Au(PPh_3)Cl$. in a standard CD_2Cl_2 solution of PPh_3 capped AuNPs. After 30 min, the nanoparticles were recovered by drying out CD_2Cl_2 with nitrogen gas. The resulting



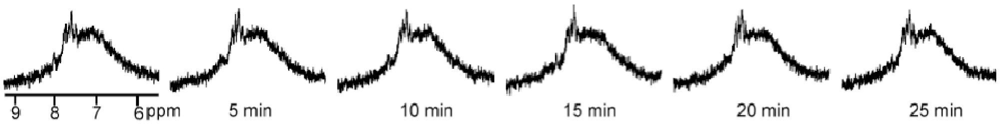
S5 ^2H solution NMR of (A) d_{15}-PPh_3 capped gold nanoparticles and (B) d_{15}-PPh_3

black powder wad re-dissolved in chloroform and precipitated with pentane to remove any exchanged unbound PPh_3 ligands. The ^2H NMR spectra were collected on a 500 MHz Varian spectrometer using the deuterium lock channel (^2H frequency = 76.7 MHz). Spectra were collected without locking the field and the B_o field homogeneity was optimized by performing gradient shimming. ^2H solution-state NMR of (A) d_{15}-PPh_3 capped AuNPs and (B) pure d_{15}-$AuPPh_3Cl$ in CH_2Cl_2 solution are shown in figure S5. The peak at 7.5 ppm is due to d_{15}-$Au(PPh_3)Cl$ and peak at 5.3 ppm is methylene chloride solvent and is used as an external reference (5.3 ppm). The broad resonance in figure S5-A is assigned to d_{15}-PPh_3 bound to the AuNP surface.

Ligand exchange of PPh_3 capped AuNPs monitored by ^1H solution NMR. Ligand exchange of PPh_3 capped AuNPs was monitored by ^1H NMR experiment on a 400 MHz Varian instrument. Evolution of $Au(PPh_3)Cl$ after addition of 72 mg d_{15}-PPh_3 in a solution prepared by dissolving 15 mg of 1.8 nm AuNPs in 1 ml CD_2Cl_2 is monitored. In figure S6, we show the ^1H solution-state NMR of PPh_3 capped AuNPs (A) before and (B) after ligand exchange. The broad ^1H NMR resonance centered at 7.1 ppm in figure S6-A is a result of heterogeneous broadening of the PPh_3 ligand bound to gold nanoparticles, while the narrow resonance at 7.5 ppm is solution phase $AuPPh_3Cl$ complex. Figure S6-B shows a large increase in PPh_3 in fast exchange with $AuPPh_3Cl$ complex, with the complete loss of PPh_3 bound to the gold nanoparticle surface, indicating that all the original PPh_3 ligands bound to the nanoparticle surface have been exchanged with d_{15}-PPh_3 surface bound ligands.



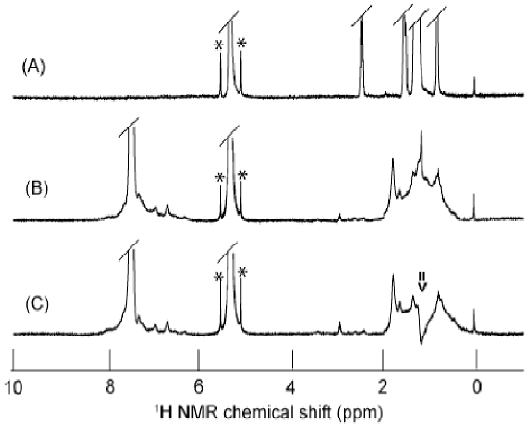
S6. (A) ^1H NMR of 15 mg of purified PPh_3 capped 1.8 nm AuNPs dissolved in 1 ml of CD_2Cl_2 at room temperature. (B) ^1H NMR spectrum 30 min after the addition of 72 mg of d_{15}-PPh_3 to solution-A.



S7. ^{1}H NMR of PPh_3 capped gold nanoparticles in CD_2Cl_2 solution. Spectra are horizontally stacked as a function of time nanoparticles spent in NMR solution after dissolving.

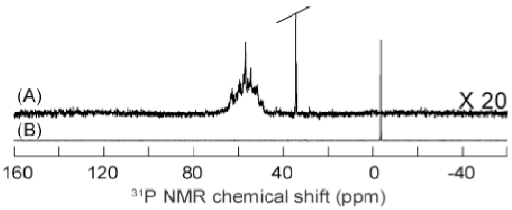
Dissociation of Au(PPh_3)Cl complex from the nanoparticles in CD_2Cl_2: The dissociation of Au(PPh_3)Cl from AuNPs was monitored by ^{1}H NMR in CD_2Cl_2. PPh_3 capped AuNP solutions were prepared by rapidly dissolving 4.0 mg nanoparticles in 1.0 ml solvent and immediate monitoring by ^{1}H NMR. The resulting data are shown in figure S7 for the first 25 minutes. It is apparent that the Au(PPh_3)Cl complex does not dissociate from the AuNPs in the time scale under which exchange kinetics is observed. However, on a longer time period, over the course of days, Au(PPh_3)Cl does dissociate from the dissolved nanoparticles as shown in figure S4.

Ligand exchange in AuPPh_3 NPs by using 1-Octanethiol. A ligand exchange reaction was performed by mixing 1-octanethiol and PPh_3 capped AuNPs in a 1:1 mole ratio of 1-octanethiol. ^{1}H NMR was acquired (A) before and (B) ten hours after ligand exchange as shown in figure S8. ^{1}H NMR spectra were acquired on a 500 MHz Varian instrument using a standard single pulse experiment. The resulting data are shown in figure S8 and agrees with results from previous reports.[2] Figure S8-C shows the broad line resonance due to surface bound 1-octanethiol is heterogeneous by hole-burning NMR experiment. The chemical shift heterogeneity is due to presence of chemically distinct environments at the nanoparticle surfaces. The frequency of the hole burned is indicated by an arrow (⇓) in figure S8-C. 1-octanethiol shows methyl peak at 0.9 ppm and methylene peaks



S8. ^{1}H NMR of (A) pure 1-octannethiol in CD_2Cl_2 (B) after ligand exchange of PPh_3 capped AuNPs with 1-octannethiol in CD_2Cl_2 and (C) hole burning NMR experiment prior to detection. Asterisks denote ^{13}C-^{1}H satellite peaks between 1 to 2 ppm. The sharp peak around 7.5 ppm in S8-B and S8-C is from Au(PPh_3)Cl being displaced from the surface of the AuNPs as a result of 1-octanethiol ligand exchange.

^{31}P NMR for quantification of observed signal from PPh_3 capped AuNPs. In order to determine whether all the ^{31}P NMR signals associated with surface bound PPh_3 were detected or not, we performed quantitative ^{31}P solution NMR of PPh_3 and PPh_3 capped AuNPs dissolved in CD_2Cl_2 separately and results are shown in figure S9. Spectra of both samples were collected using identical NMR experimental conditions on a 500 MHz Varian instrument. A full 5*T_1 delay time of 65 seconds was used between transients to ensure a complete return to equilibrium. We used equal moles of PPh_3 as established from TGA results shown in figure S2, allowing for quantitative analysis of ^{31}P NMR. Comparison of quantitative integrated areas of the ^{31}P NMR from these the ^{31}P NMR from these spectra insured that all signal associated with surface bound PPh_3 ligands were detected.



S9. Quantitative ^{31}P{H} solution NMR of (A) 15 mg PPh_3 capped AuNPs and (B) 3 mg PPh_3 taken under identical NMR experimental conditions.

References

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(2) Woehrle, G. H.; Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 2172-2183.