Electronic Supplementary Information for Dalton Transactions

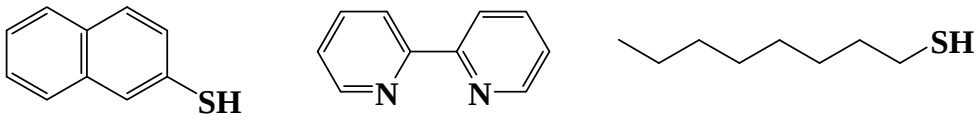
-Supporting Information-

Probing the Kinetics of Ligand Exchange on Colloidal Gold Nanoparticles by Surface-Enhanced Raman Scattering

*Yuhua Feng, Shuangxi Xing, Jun Xu, Hong Wang, Jun Wei Lim, and Hongyu Chen**

Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore 637371

Email: hongyuchen@ntu.edu.sg



1 **2** **3**

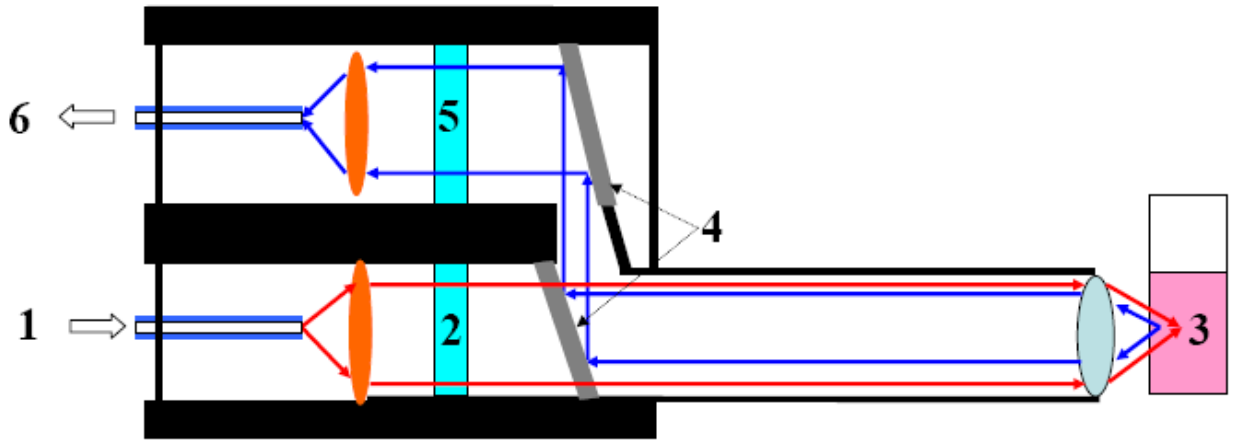
Scheme S1. Ligands used in the study: **1**, 2-naphthalenethiol; **2**, 2, 2′-bipyridine; **3**, 1-octanethiol.

Experiment section

All solutions were prepared using ultrapure water (resistivity > 18 MΩ·cm^{-1}). 2-naphthalenethiol (99%, Aldrich), 2,2′-bipyridine (98%, Fluka), 1-octanethiol (≥98.5%, Aldrich), Hydrogen tetrachloroaurate(III) (99.9%, Au 49% on metals basis, Alfa Aesar), sodium citrate tribasic dihydrate (99.0%, Sigma), ethanol (99.9%, TEDIA Company. INC.), and dimethylformamide (DMF, 99.8%, TEDIA Company. INC.) were used as received. Copper specimen grids (200 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Electron Microscopy Sciences. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 ~ 120 kV. Raman spectra were collected from sample solutions in a quartz cuvette (pathlength = 1.00 cm) on an R-3000 spectrometer (Raman Systems Inc.) using red LED laser (λ = 785 nm) at 290 mW. Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer.

Raman spectra collection and data processing.

The R-3000 Raman spectrometer was equipped with a 785 nm LED laser, and the power was set to 290 mW. Both the integration time and the frame size were set to 30 seconds. Raman measurement was performed as shown in Scheme S2: 600 μL sample solution of citrate-AuNPs in DMF (87 pM) was added into a 1.5 mL quartz cuvett (pathlength = 1.00 cm). Then, a ligand solution was added and the solution was mixed homogeneously by pipetting up and down. The cuvette was quickly placed into the sample holder and the data collection was started immediately afterwards. For convenience, the time at the collection of first spectra was set as 0 min.



Scheme S2 Diagram of the R-3000 Raman spectrometer: 1) 785 nm laser in; 2) clean up filter for 785 nm laser; 3) Sample solution; 4) Dichromic mirror: separate 785 nm laser and the Stoke-shifted Raman signal; 5) filter: remove 785 nm laser; 6) Raman signal output.

To monitor the aggregation state of AuNPs, UV-vis spectra were recorded before the addition of ligand and after the end of Raman measurements. If aggregation had occurred, a broad absorption will appear at 600-800 nm, in addition to the original plasmon absorption at ~ 540 nm. If the aggregation were serious, the color of the solution will also turn blue.

For data processing, we use 'peak height' to monitor the changes in Raman signals at different time intervals; all Raman intensities reported in this work are calculated using this method. The formula is: Peak Height ≅ $y_1 - (y_2 + y_3)/2$ (Fig. S1).

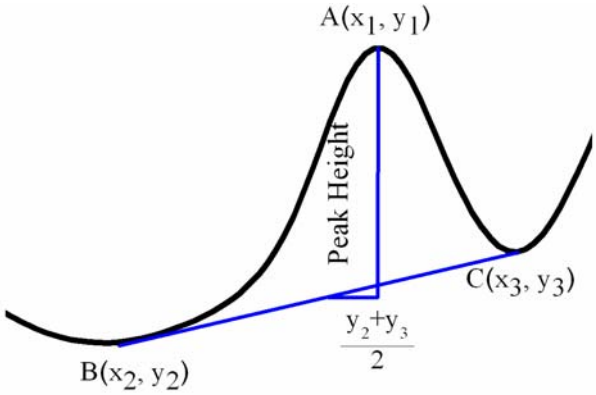


Fig. S1. The calculation of Raman peak height.

Synthesis of Au nanoparticles (AuNPs) (d_{av} = 18 and 64 nm).

The medium AuNPs (d_{av} = 18 nm) were prepared by the citrate-reduction method.[1] The large AuNPs (d_{av} = 64 nm) were synthesized by a seeded growth method adapted from the citrate-reduction method. In a typical procedure, 1 mL $HAuCl_4$ solution (10 mg/mL) was added to 90 mL H_2O in a 250 mL round bottle flask equipped with condenser and refluxed for 30 minutes. Then, a mixture of 1.5 mL AuNPs (d_{av} = 18 nm) seed and 0.4 mL sodium citrate solution (1% wt) was added into the boiling $HAuCl_4$ solution. After stirring for a few minutes, the color of solution changed from light yellow to black and then to purple. About 20 minutes later, the solution changed to red and is very clear. This solution was heated for a total of 1.8 hrs, and allowed to cool down in the oil bath till room temperature. The average diameter of AuNPs measured from TEM was about 64 nm and the estimated concentration of the as-synthesized AuNPs is 35.2 pM.

Purification of AuNPs.

A citrate-AuNPs solution (1.5 mL) was concentrated to a total of 13 μL by centrifugation (at 4000 rpm (1300 *g*) for d_{av} = 64 nm AuNPs). After removing the supernatant, the concentrated

AuNP solution was diluted by 1.5 mL DMF, centrifuged for the second time and then redispersed in DMF. The concentration of AuNPs at this stage was estimated by comparing the absorption peak intensity of the solution with that of the as-synthesized solution.

Experiment of ligand adsorption and ligand exchange reactions.

For ligand exchange with citrate-AuNPs, a DMF solution of ligand (0.5 μL of **1**, or 20 μL of **2**) was added to a 1.5 mL cuvette containing 600 μL citrate-AuNPs in DMF (d_{av} = 64 nm, 87 pM). This solution was mixed by pipetting up and down and then quickly placed into the sample holder for sequential Raman measurements. In the reaction mixture, $[\mathbf{1}]_{total}$ = 10 μM, or $[\mathbf{2}]_{total}$ = 0.4 mM.

For ligand exchange with **1**-AuNPs, a DMF solution of **3** (40 μL) was added to a 1.5 mL cuvette containing 600 μL **1**-AuNPs in DMF (d_{av} = 64 nm, [AuNP] = 87 pM, $[\mathbf{1}]_{total}$ = 2 μM, pre-incubated overnight). This solution was mixed by pipetting up and down and then quickly placed into the sample holder for sequential Raman measurements. In the reaction mixture, $[\mathbf{3}]_{total}$ = 0.9 mM.

Before and after kinetic experiments, UV spectra of the samples were recorded to examine the aggregation state of the AuNPs.

Encapsulation of AuNPs in PS_{154}-*b*-PAA_{60} using 1 as ligand.

This method was modified from our previously published procedures.[2]

The **1**-AuNPs (d_{av} = 64 nm) obtained from the kinetic experiments were in DMF (600 μL) solutions, with varying $[\mathbf{1}]_{total}$. Two solutions, one with high $[\mathbf{1}]_{total}$ (0.2 mM) and one with low $[\mathbf{1}]_{total}$ (0.01 μM), were selected for this test. To each of these solutions was added 400 μL DMF (so that V_{DMF} = 1 mL), a solution of PS_{154}-*b*-PAA_{60} (80 μL, 8 mg/mL in DMF), and then finally a solution of **1** in DMF (in varying amounts, so that the total **1** equals 0.5 μmol). Then, 250 μL H_2O were added to this solution, so that the DMF:H_2O = 4.5:1. The total volume of the final mixture was 1120 μL, where the DMF/H_2O volume ratio was 4.5, [**1**] = 0.4 mM, and [PSPAA] = 0.03

mM. The mixture was heated at 110 °C for 2 hrs in an oil bath and then allowed to slowly cool down to room temperature.

The samples were then purified for TEM characterization: For both samples, an aliquot (0.3 mL) was diluted by 1.2 mL H_2O and then centrifuged to remove the supernatant. The deep red suspension collected at the bottom of eppendorf tubes was used for TEM.

Calculations:

Equivalent of $HAuCl_4$ from the 15 nm AuNPs seed = 0.13 mg

Total weight of $HAuCl_4$ in the as-synthesized 64 nm AuNP solution = 8.86 mg

Total weight of Au in the as-synthesized 64 nm AuNP solution = 5.07 mg

Weight of each 64 nm AuNP = $\rho_{Au} \times V_{AuNP} = 2.6 \times 10^{-12}$ mg

Number of AuNPs in 92 mL 64 nm AuNP solution = 5.07 mg / 2.6×10^{-12} mg = 1.95×10^{12} = 0.324×10^{-11} mol

Concentration of as-synthesized 64 nm AuNP solution = 0.324×10^{-11} mol / 0.092 L = 3.52×10^{-11} M = 35.2 pM

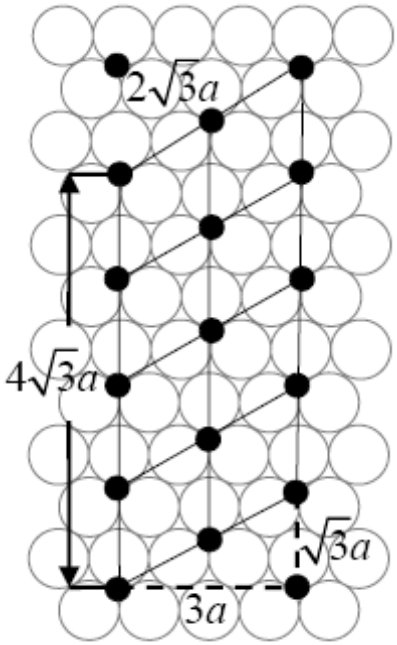
Concentration of the purified AuNPs in 600 μL DMF (based on UV-vis absorption at 540 nm) = 87 pM

Surface area of each AuNP = $4\pi(d/2)^2 = 12717.16$ nm^2

Surface area of a 2D unit cell with 8 Au binding sites = 1.724 nm^2 (see reference 3)

Number of Au binding sites on each AuNP = (12717.16 nm^2 / 1.724 nm^2) × 8 = 59012

Equivalent concentration of Au binding sites in the DMF solution = 87 pM × 59012 = 5.13 μM



Scheme S3 Diagram of binding sites on the (111) surface of AuNPs (a = 2.88 Å), as based on ref. 3.

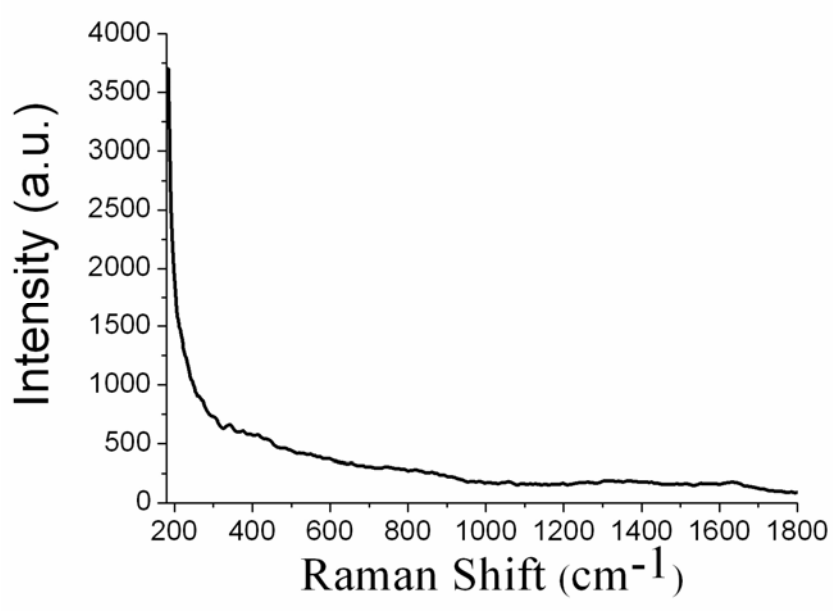


Fig. S2. Raman spectra of Citrate-AuNP in H_2O.

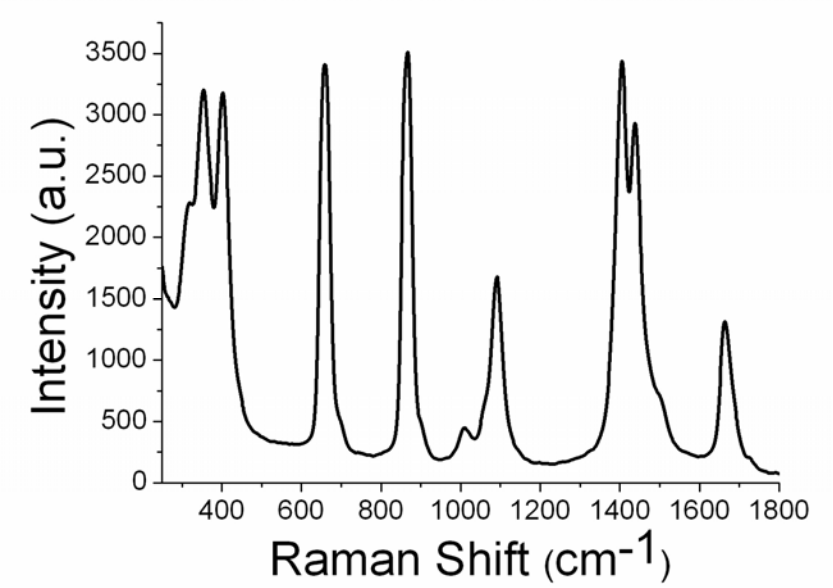


Fig. S3. Raman spectra of Citrate-AuNP dispersed in DMF.

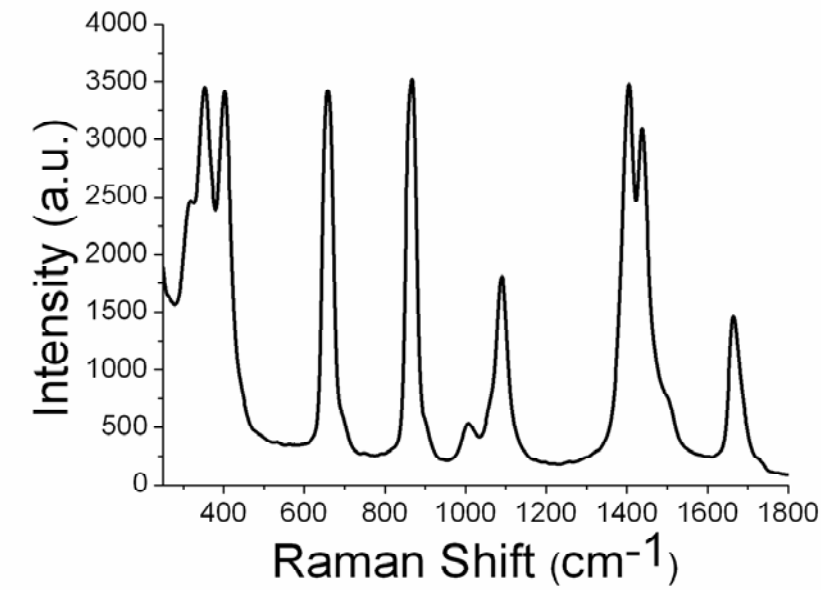


Fig. S4. Raman spectra of PSPAA (8 mg/mL) in DMF.

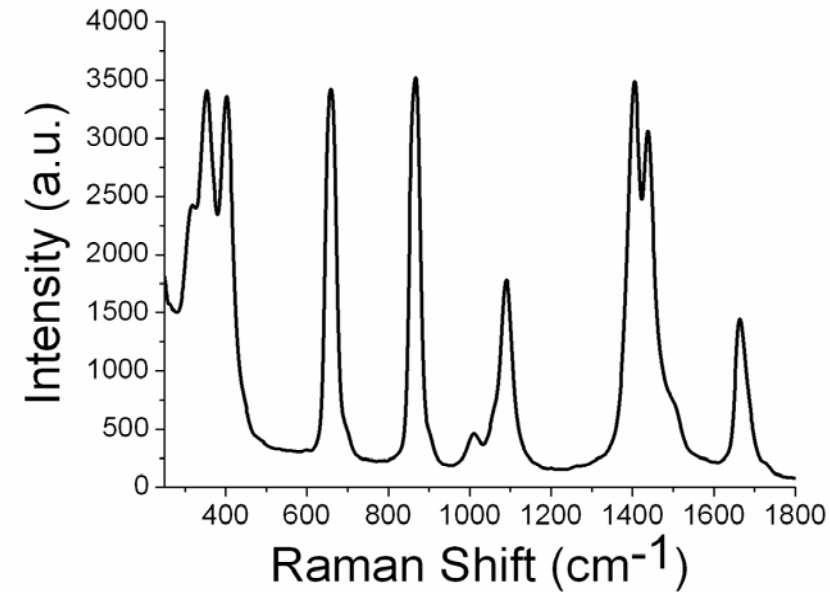


Fig. S5. Raman spectra of pure DMF.

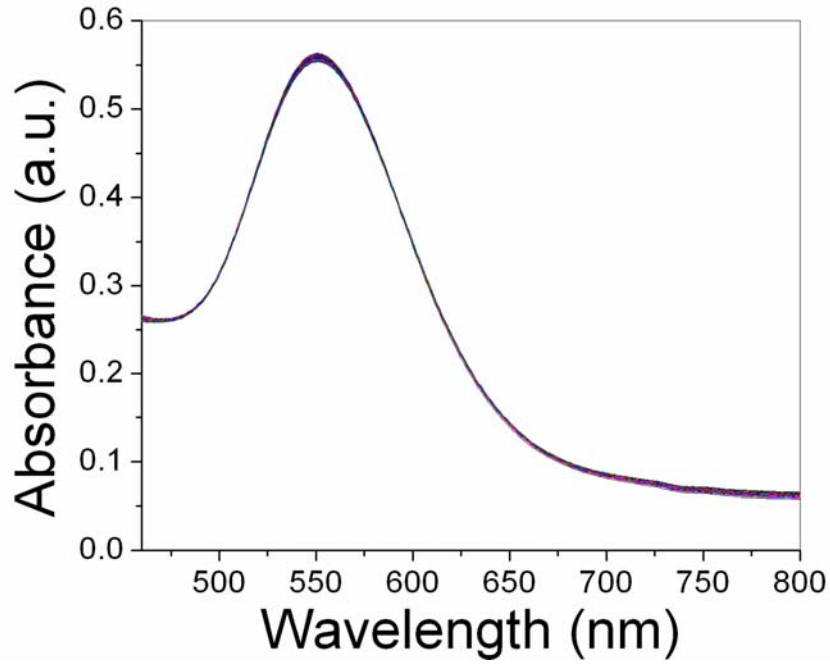


Fig. S6. UV-Vis-based kinetic study of purified citrate-AuNP (87 pM) incubated with **1** (0.4 mM) in DMF at room temperature for 3 h, showing the overlapped view of 163 spectra. This indicated that no aggregation occurred during and after the ligand coordination.

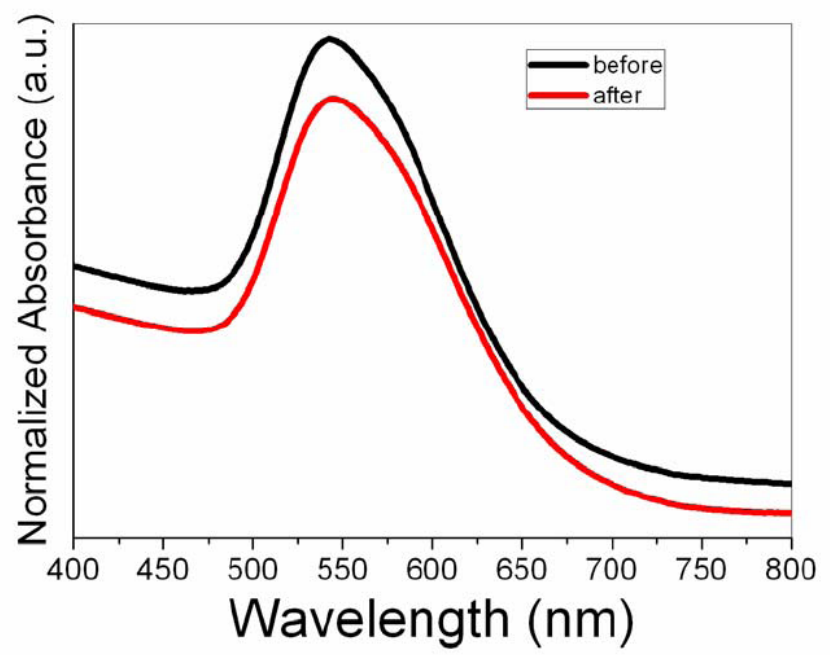


Fig. S7. UV-Vis spectra of citrate-AuNP (87 pM) before and after incubated with **1** (10 μM) in DMF. The 2nd spectrum was displaced in order to compare the shapes of the two spectra.

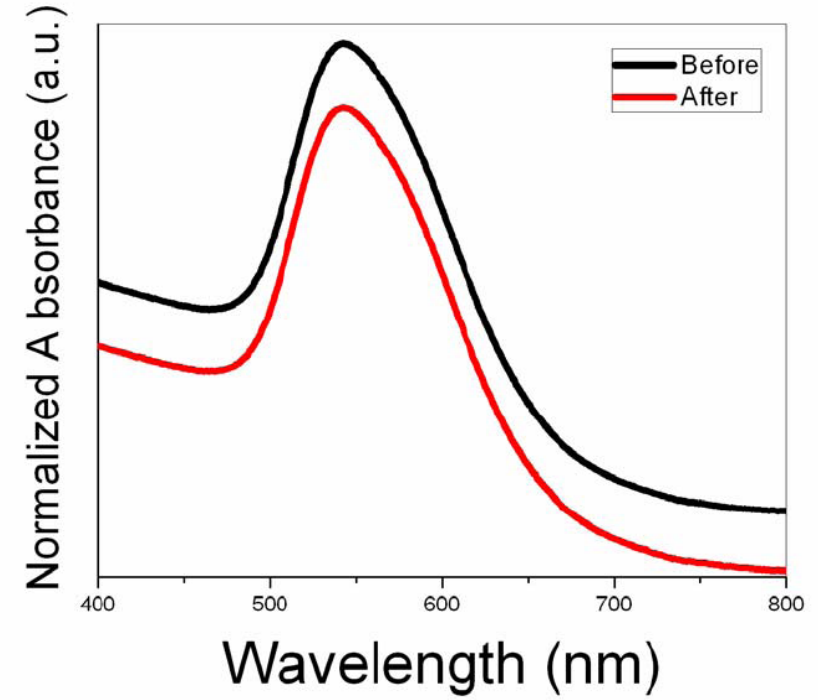


Fig. S8. UV-Vis spectra of citrate-AuNP (87 pM) before and after incubated with **2** (0.4 mM) in DMF. The 2nd spectrum was displaced in order to compare the shapes of the two spectra.

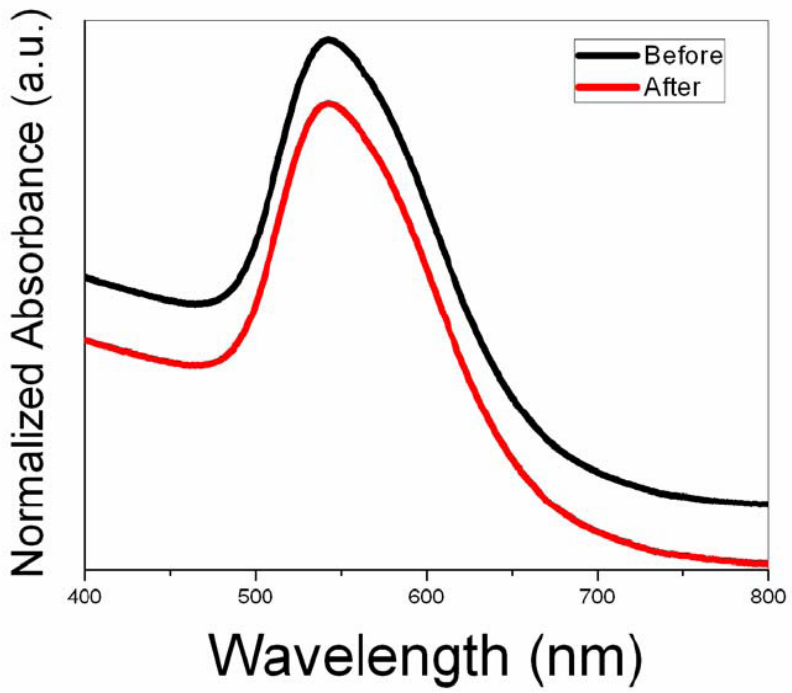


Fig. S9. UV-Vis spectra of citrate-AuNPs (87 pM) before and after incubated with **1**, ($[\mathbf{1}]_{total}$ = 0.02 μM) in DMF. The 2nd spectrum was displaced in order to compare the shapes of the two spectra.

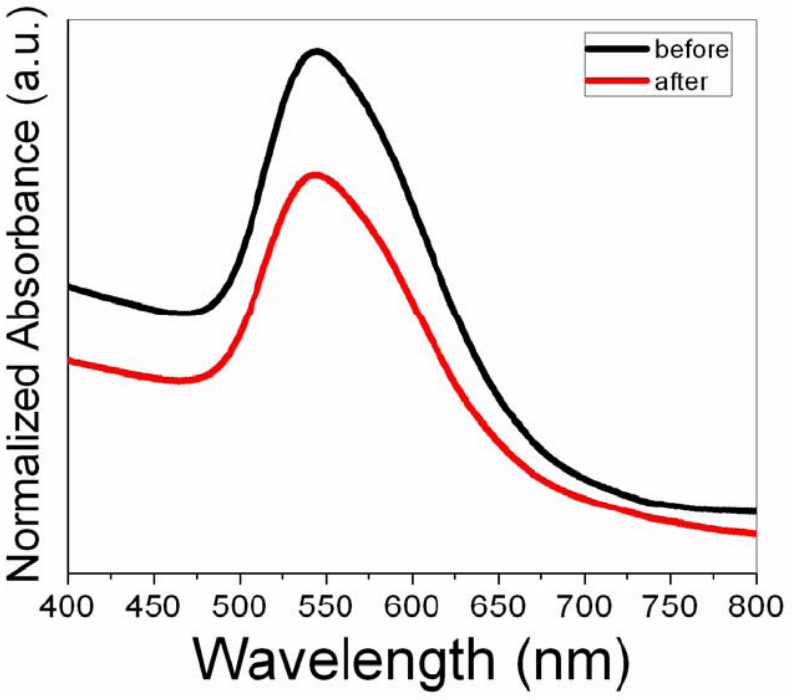


Fig. S10. UV-Vis spectra of **1**-AuNP ([AuNPs] = 87 pM, $[\mathbf{1}]_{total}$ = 2 μM) before and after incubated with **3** ($[\mathbf{3}]_{total}$ = 0.9 mM) in DMF. The 2nd spectrum was displaced in order to compare the shapes of the two spectra.

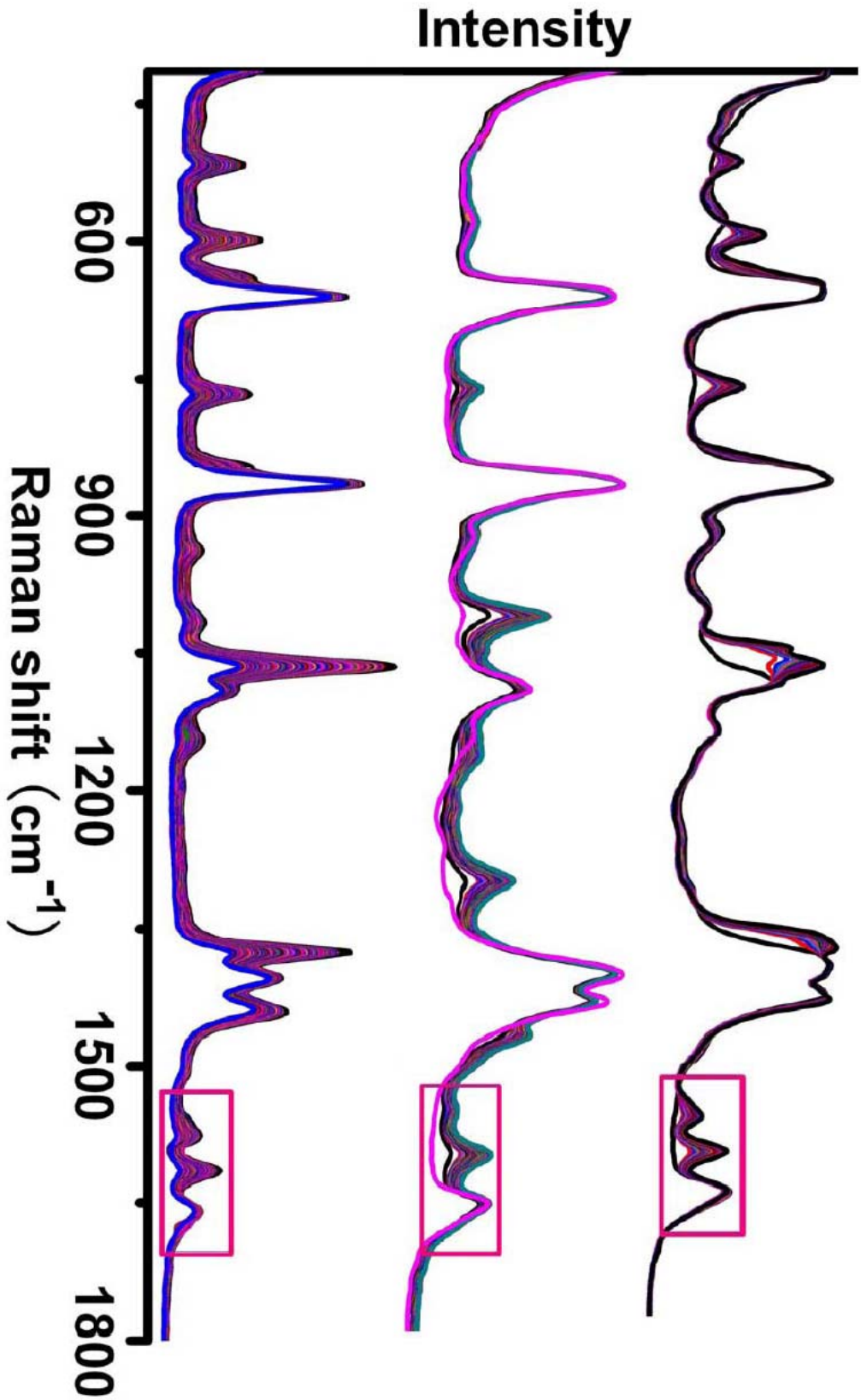
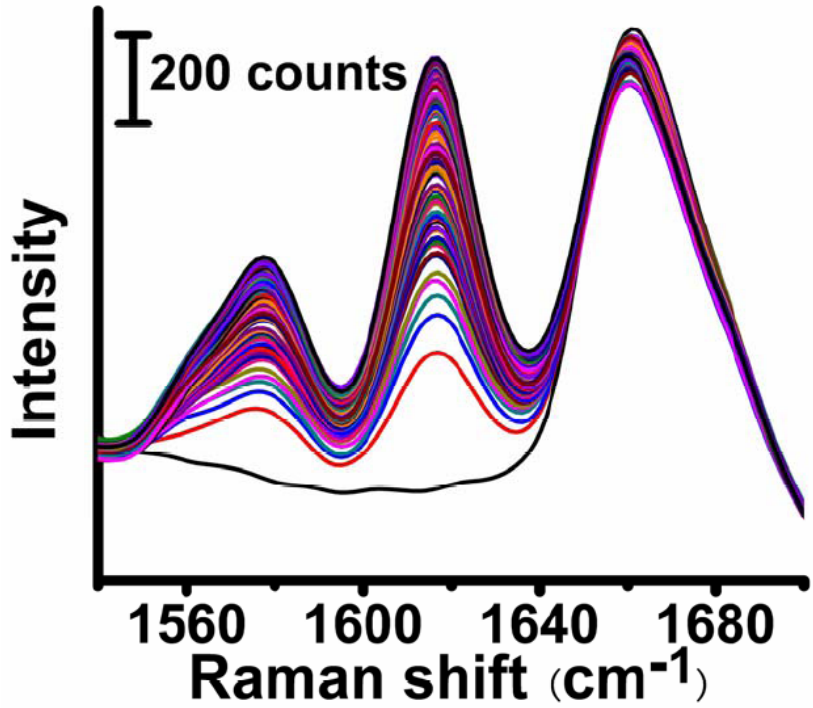
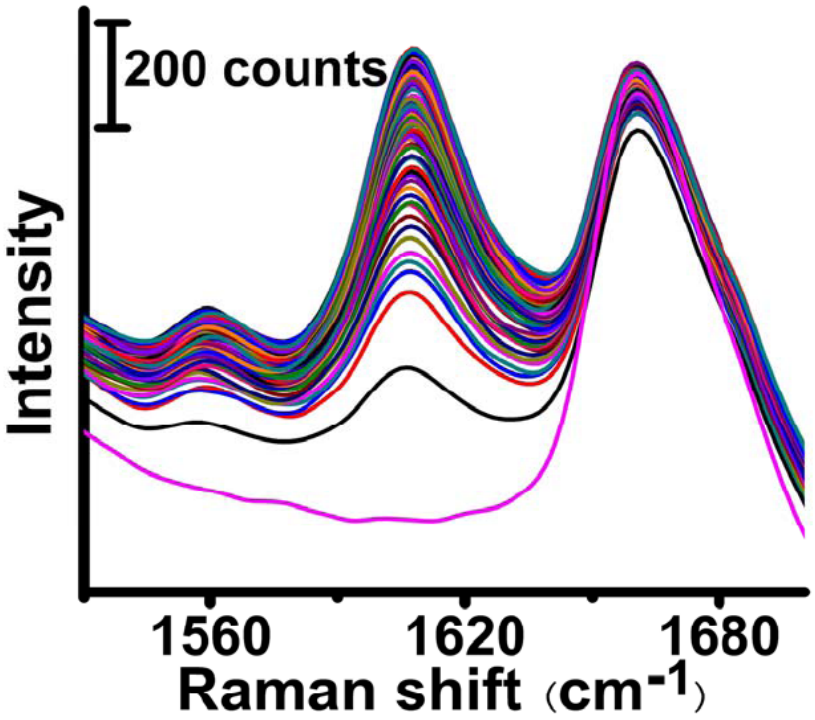


Fig. S11 Enlarged views of Fig. 1c, 3a and 3d





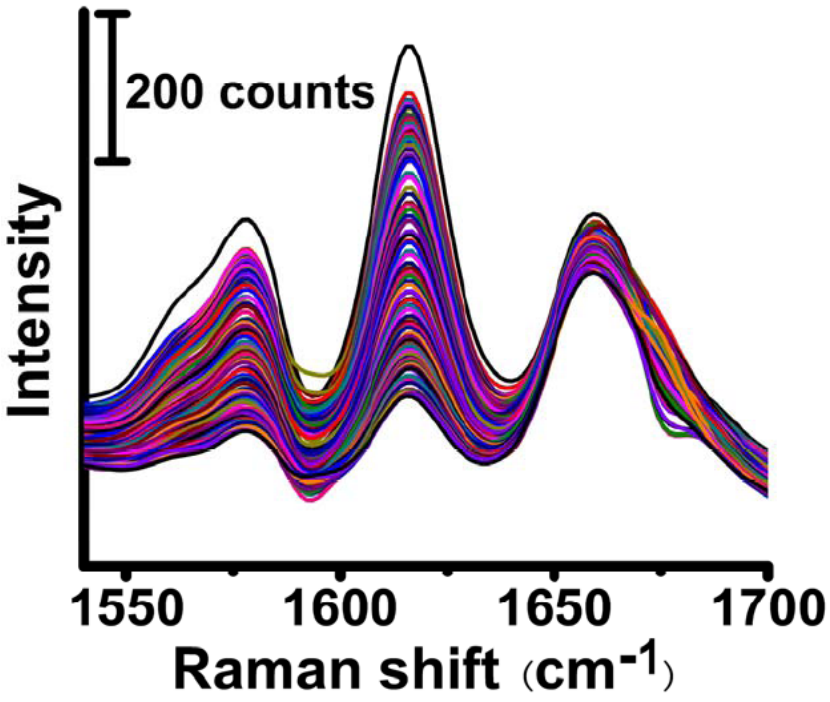


Fig. S12. Enlarged views of the framed region in Fig. 1e, 3c and 3f.

References

1. G. Frens, *Nature Phys. Sci.*, 1973, 241, 20.

2. M. X. Yang, T. Chen, W. S. Lau, Y. Wang, Q. H. Tang, Y. H. Yang and H. Y. Chen, *Small*, 2009, 5, 198; H. Y. Chen, S. Abraham, J. Mendenhall, S. C. Delamarre, K. Smith, I. Kim and C. A. Batt, *ChemPhysChem*, 2008, 9, 388.

3. J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, 105, 1103.