Electronic Supplementary Information

Facile Preparation of Size-controlled Gold Nanoparticles Using Versatile and End-functionalized Thioether Polymer Ligands

Xin Huang,[a] Buyi Li,[a] Hui Zhang,[a] Irshad Hussain,[b] Liyun Liang[a] and Bien Tan*[a]

Contents:

S-Ⅰ Thioether polymer ligands characterization

Gel Permeation Chromatography. GPC was performed with an Agilent 1100 instrument using refractive index detector (RID) in order to obtain the molecular weights of polymer ligands. THF was used as the eluent at a flow rate of 1.0 mL/min at 23 ℃. The calculated molecular weights were based on a calibration curve for polystyrene standards of narrow polydispersity (Polymer Laboratories).

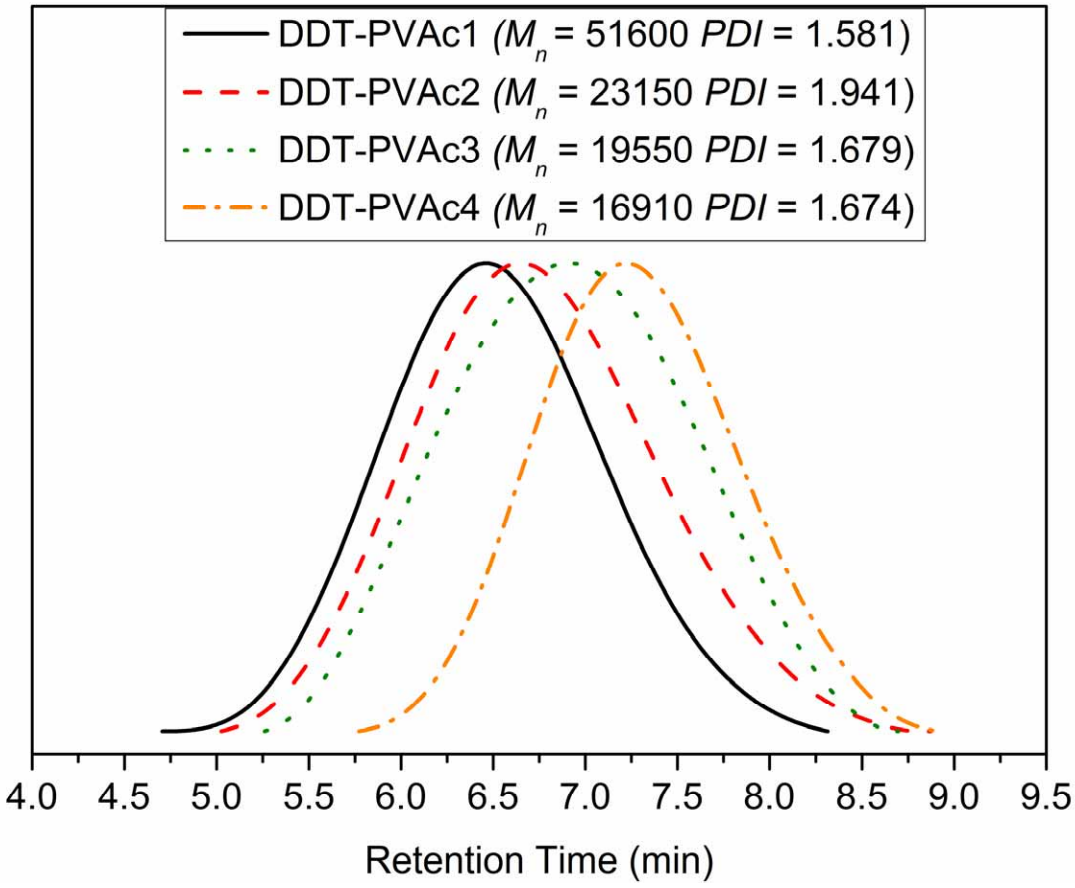


Figure S1 GPC elution curves of thioether polymer ligands DDT-PVAc with different molecular weights (red curve: DDT-PVAc1, olive curve: DDT-PVAc2, black curve: DDT-PVAc3, orange curve: DDT-PVAc4).

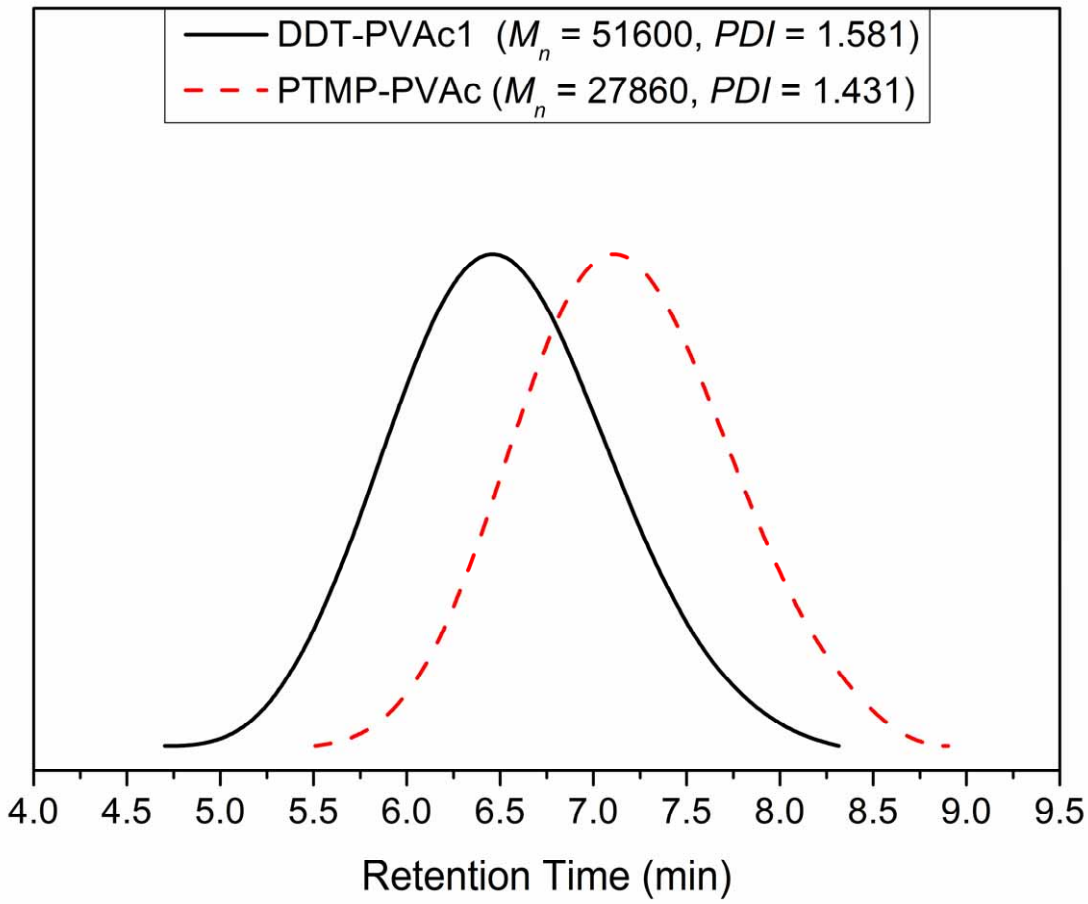


Figure S2 GPC elution curves of thioether polymer ligands DDT-PVAc and PTMP-PVAc with the equal molar ratio of chain transfer agent (black curve: DDT-PVAc1, red curve: PTMT-PVAc).

S-‖ The characterization of Au NPs prepared by thioether polymer ligands

[1]H NMR Spectroscopy. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AV400 MHz spectrometer at room temperature using the δ scale and tetramethylsilane (TMS) as an internal standard.

DDT-PVAc ($CDCl_3$) δ (ppm): 0.86-0.89 CH_3 (from DDT), 1.25 $(CH_2)_9$, 1.72 CH_2 (backbone), 1.74-1.77 CH_2, 1.94-2.08 CH_3, 2.55 CH_2 (from DDT), 4.86 CH;

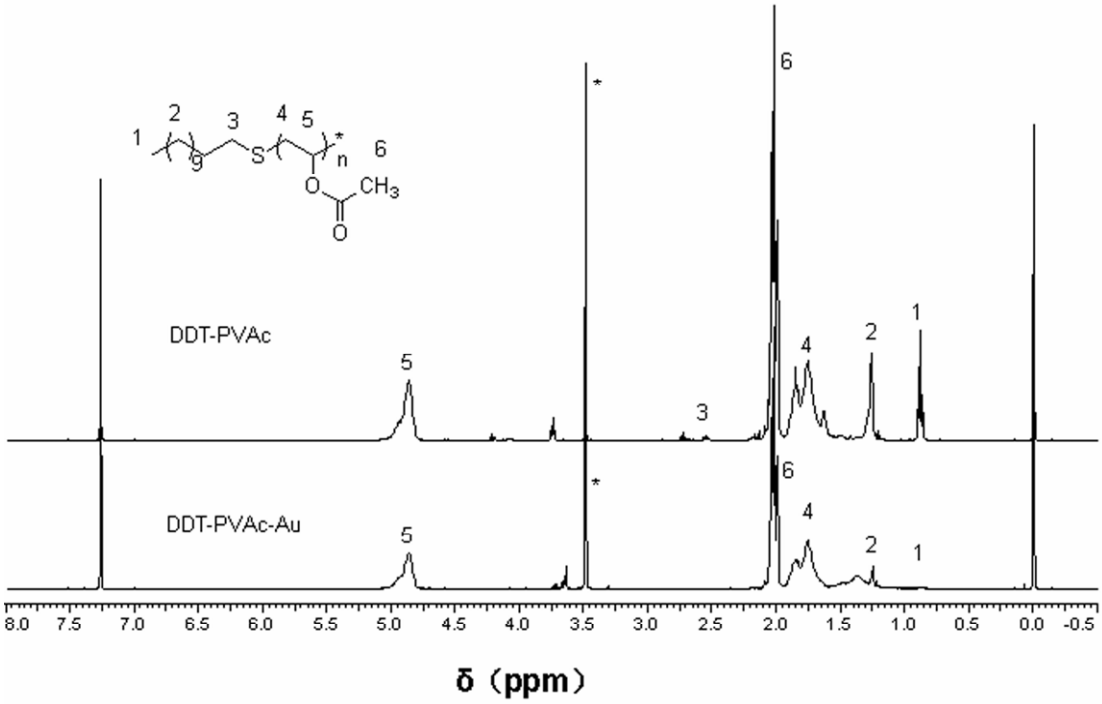


Figure S3 ^{1}H NMR of thioether polymer ligands DDT-PAVc (upper) and gold nanoparticles prepared by DDT-PAVc (lower).

PTMP-PMAA ($CDCl_3$) δ (ppm): 1.45-1.61 SH, 1.74-1.77 CH_2, 1.94-2.08 CH_3, 2.61-2.70 CH_2 (from PTMP), 2.72-2.83 CH_2 (from PTMP), 4.17-4.27 CH_2 (from PTMP), 4.86 CH.

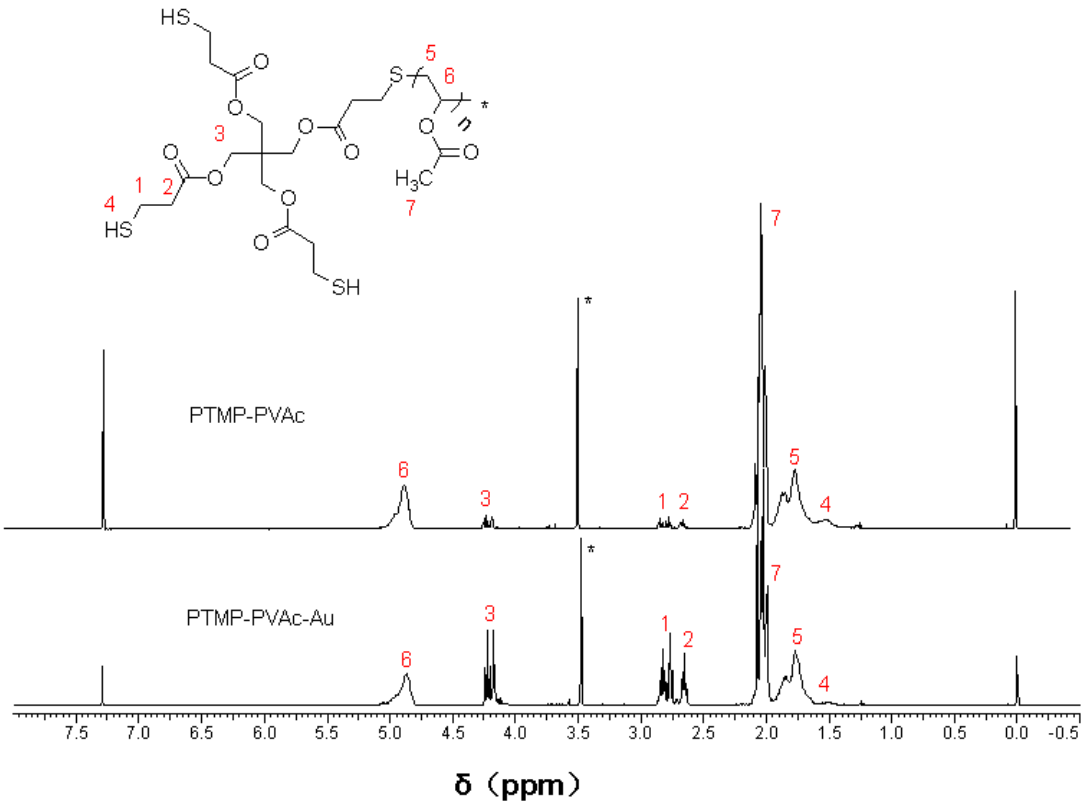


Figure S4 ^{1}H NMR of thioether polymer ligands PTMP-PAVc (upper) and gold nanoparticles prepared by PTMP-PAVc (lower).

Thermogravimetric Analysis. TGA was performed on a Pyris1 TGA purchased from PerkinElmer Instruments. The Au NPs prepared using thioether polymer ligands heated from 30 to 700 ℃ at the rate of 10 ℃/min under the nitrogen and oxygen atmosphere in the TGA pan. It was easily obtained the content of various components in the sample from the curves (weight loss vs temperature). The measured values of Au NPs contents were consistent with the theoretical values.

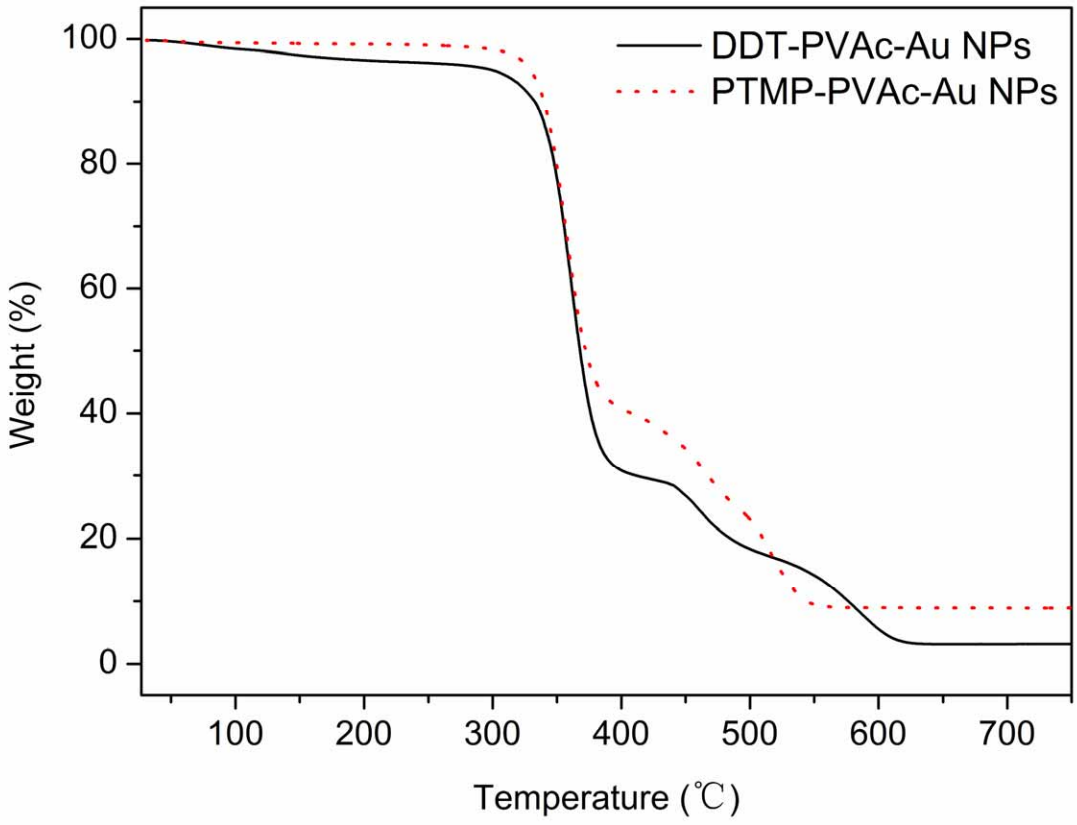


Figure S5 Weight loss versus temperature curves of DDT-PVAc protected Au NPs (black) and PTMP-PVAc protected Au NPs (red).

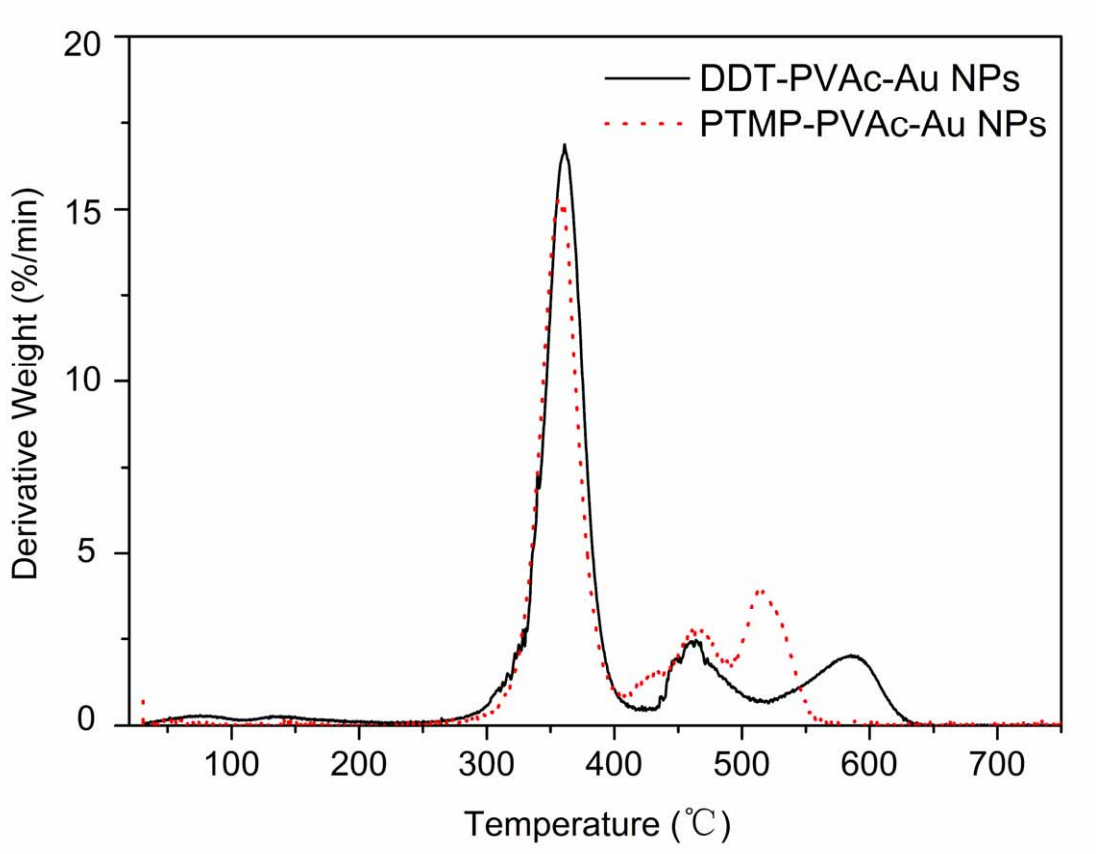


Figure S6 Derivative thermogravimetric curves of DDT-PVAc protected Au NPs (black) and PTMP-PVAc protected Au NPs (red).

Dynamic Light Scattering.

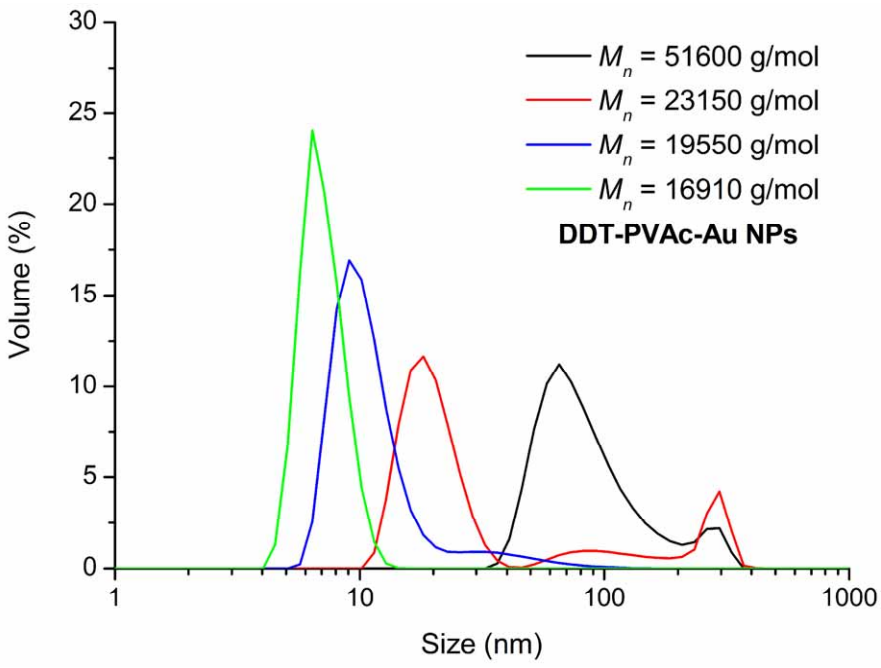


Figure S7 DLS spectra of Au NPs stabilized with monodentate ligands DDT-PVAc in toluene at different molecular weights.

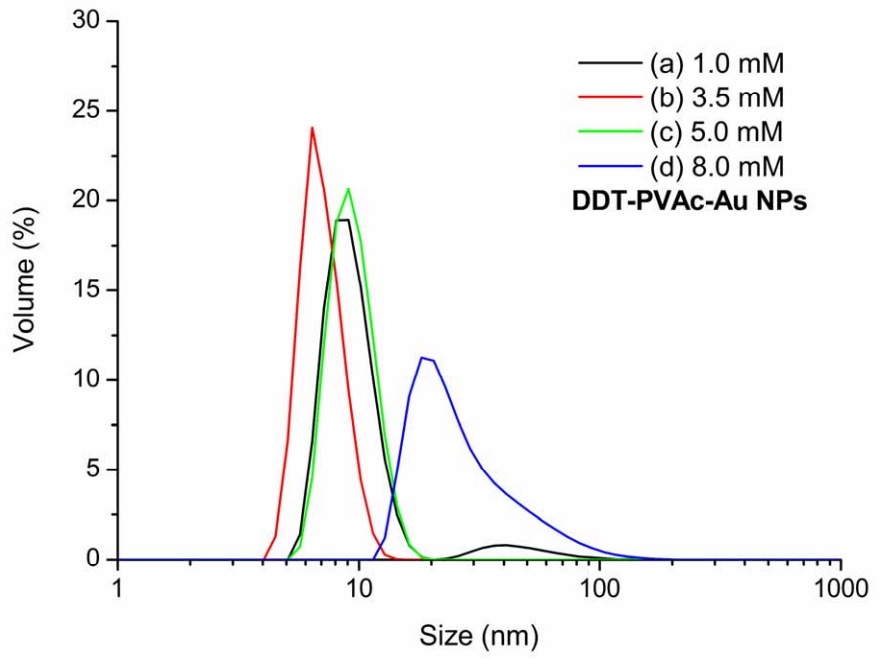


Figure S8 DLS spectra of Au NPs stabilized with monodentate ligands DDT-PVAc in toluene at different concentrations.

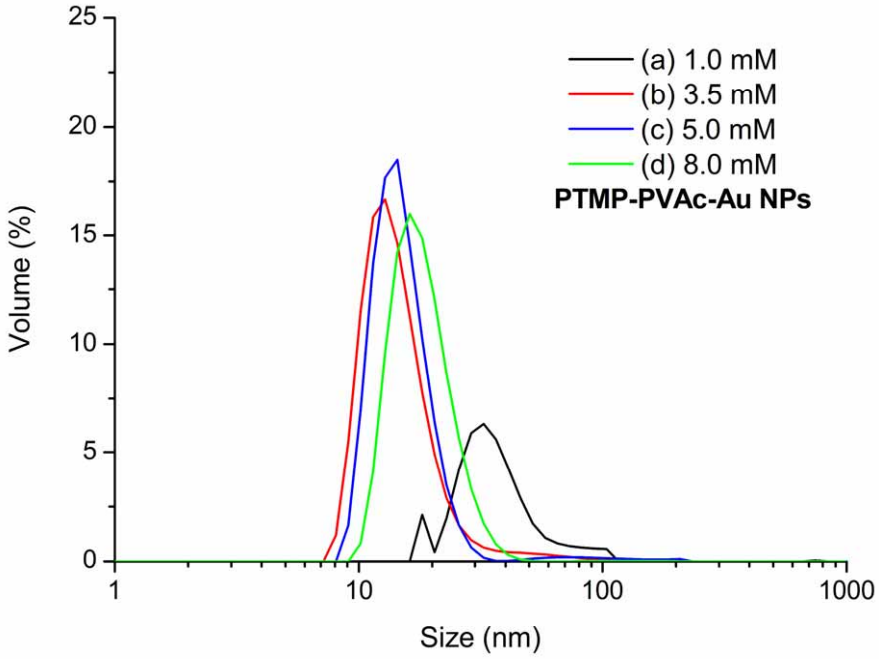


Figure S9 DLS spectra of Au NPs stabilized with multidentate polymer ligands PTMP-PVAc in toluene at different concentrations.

Size-distribution of Au NPs Prepared by DDT-PVAc at Different M_n.

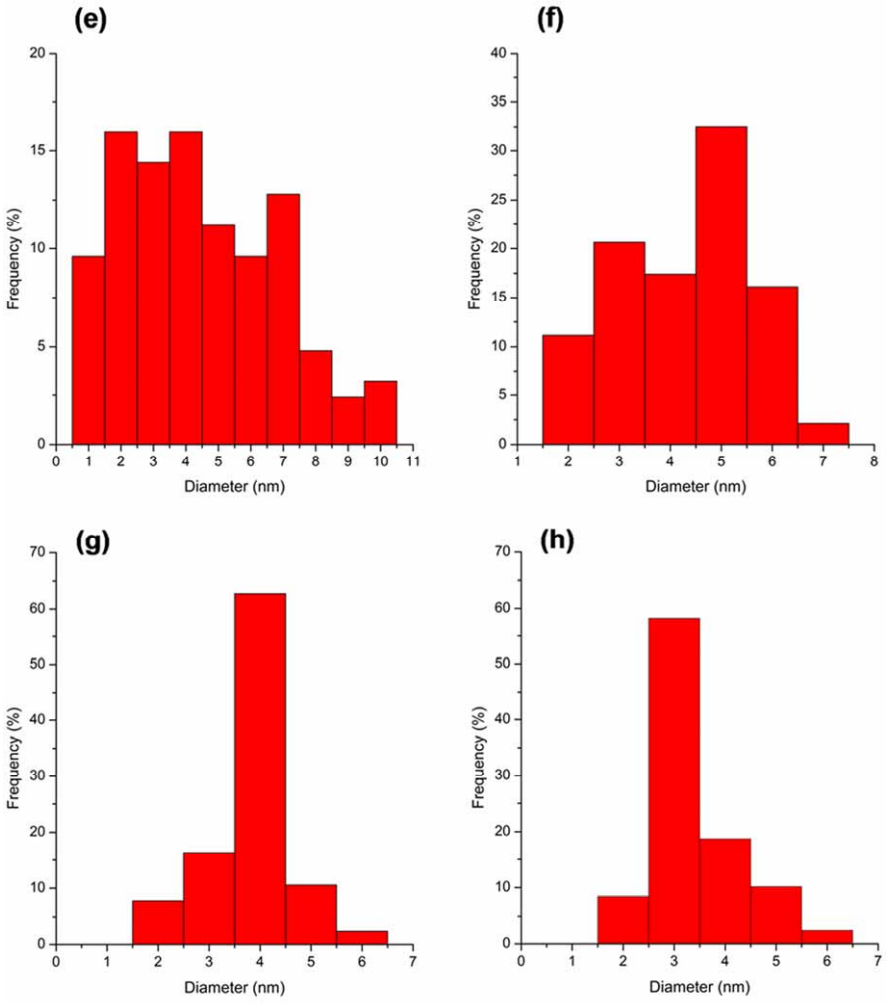


Figure S10 The histograms of the size-distribution of Au NPs prepared by four different molecular weights (M_n) of monodentate ligands DDT-PVAc. The graphs (d), (e), (f) and (g) is corresponding the Fig. 1 (a), (b), (c) and (d) respectively.

The Synthesis of Au NPs Protected by DDT. In order to compare with our synthetic method, we prepared Au NPs by classic Brust-Schiffin two-phase method using small molecular ligand dodecanethiol (DDT) at the same concentration. A solution of cetyltrimethylammonium bromide in toluene (8 mL, 50 mM) was mixed with an aqueous solution of hydrogen tetrachloroaurate (3 mL, 30 mM) and n-butanol (0.5 mL) as cosurfactant by vigorously stirring. When the cetyltrimethylammonium bromide was transferred into the organic layer totally, polymer ligand DDT (17 mg) was added to the mixture. A freshly prepared aqueous solution of sodium borohydride (2.5 mL, 0.4 mol/L) was slowly added drop wise into the system. The process of preparation was accordance with the Au NPs prepared by functional thioether polymer ligands DDT-PVAc. From TEM micrograph (Fig. S11), we can see that the particle size was not uniform. Thus our thioether polymer ligands have the advantage to form the more uniform nanoparticles as to the small molecular compounds DDT.

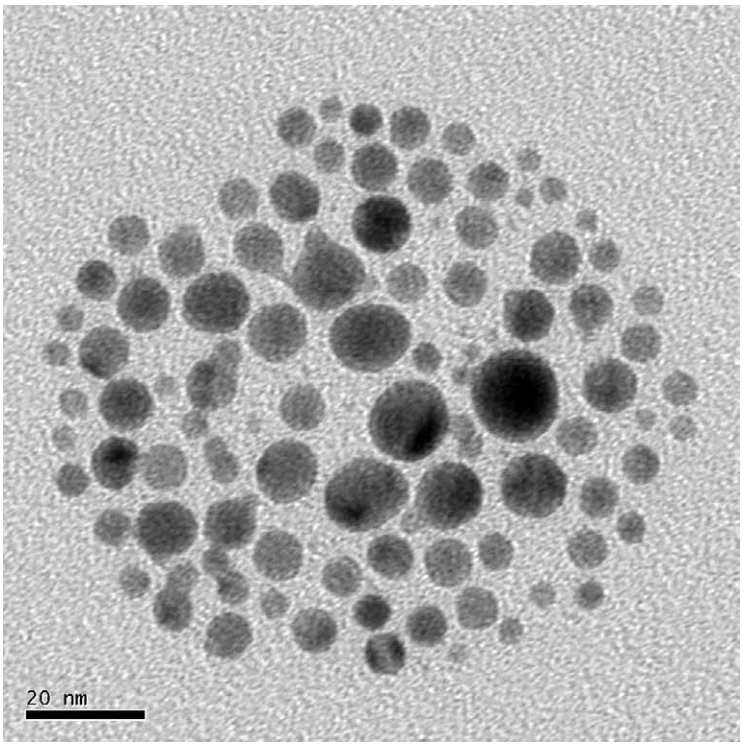


Figure S11 TEM micrographs of Au NPs prepared by small molecular compound DDT.

Size-distribution of Au NPs Prepared by DDT-PVAc at Different Concentrations.

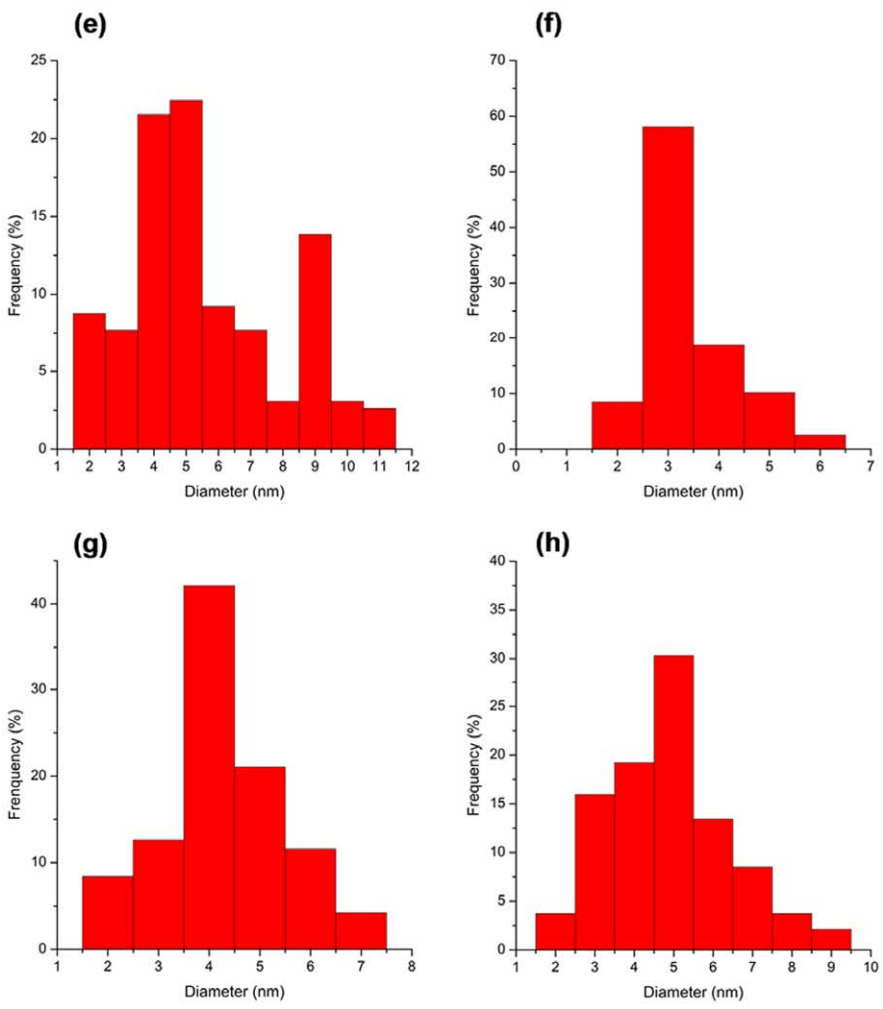


Figure S12 The histograms of the size-distribution of Au NPs prepared by four different concentrations of monodentate ligands DDT-PVAc, (a) 1.0 mM, (b) 3.5 mM, (c) 5.0 mM, (d) 8.0 mM. The graphs (d), (e), (f) and (g) is corresponding the Fig. 3 (a), (b), (c) and (d) respectively.

Size-distribution of Au NPs Prepared by PTMP-PVAc at Different Concentrations.

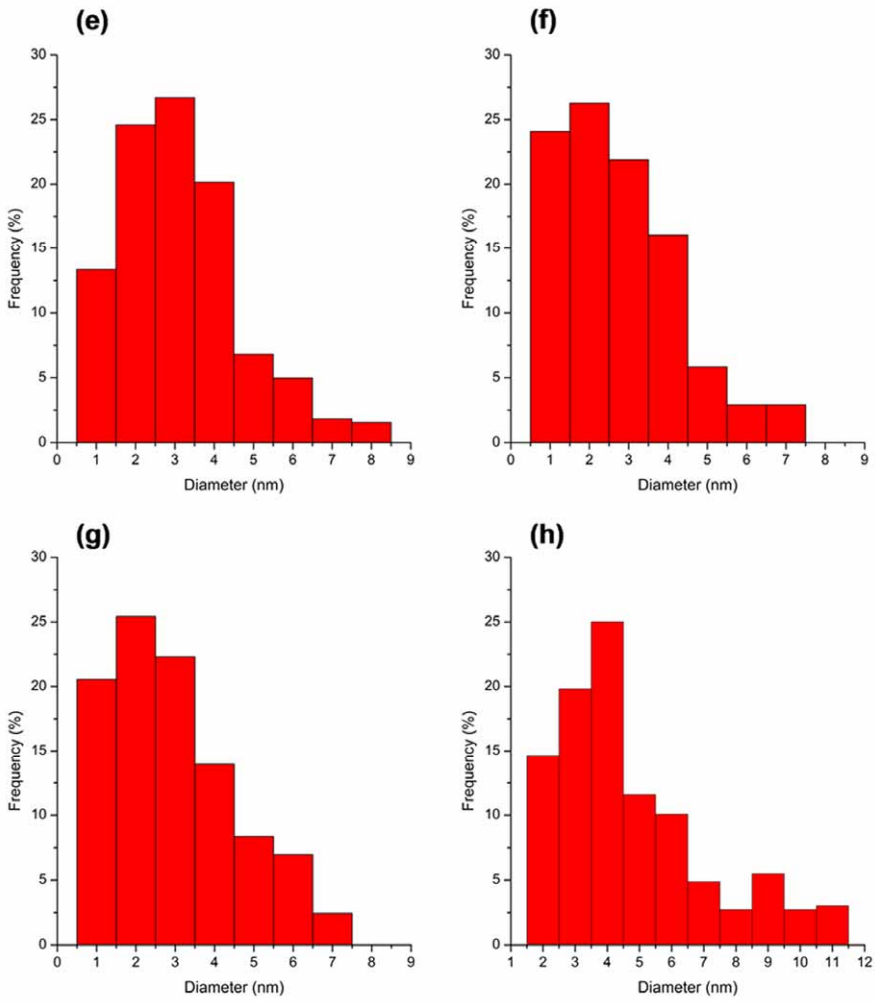


Figure S13 The histograms of the size-distribution of Au NPs prepared by four different concentrations of multidentate polymer ligands PTMP-PVAc, (a) 1.0 mM, (b) 3.5 mM, (c) 5.0 mM, (d) 8.0 mM. The graphs (d), (e), (f) and (g) is corresponding the Fig. 5 (a), (b), (c) and (d) respectively.

UV-Visible Absorption Spectroscopy.

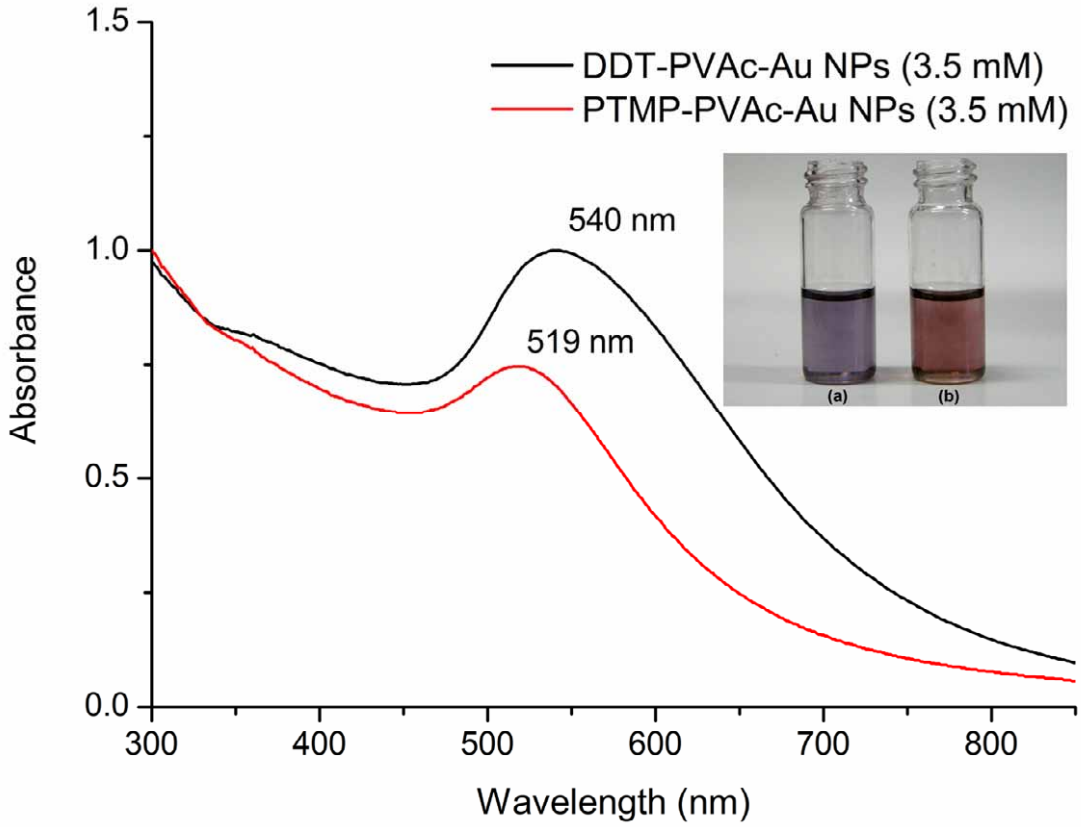
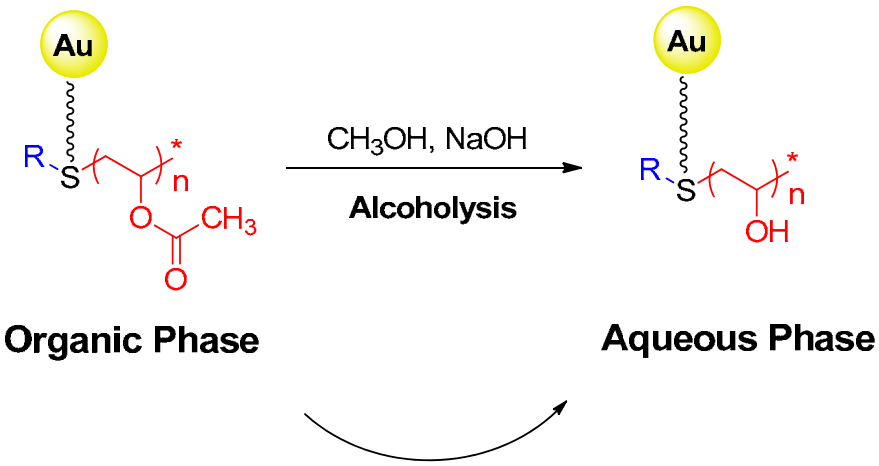


Figure S14 UV-Vis absorption spectra of Au NPs stabilized with monodentate ligands DDT-PVAc (black curve) and multidentate polymer ligands PTMP-PVAc (red curve). Insert: photograph of Au NPs prepared by monodentate ligands DDT-PVAc (a) and multidentate polymer ligands PTMP-PVAc (b).

S-|||Modification and characterization of thioether polymer ligands

Modification of Thioether Polymer Ligand. Au NPs (0.451 g) stabilized by thioether polymer ligands DDT-PVAc were dissolved into solvent methanol (6 mL) in a sealed 50 mL three-neck flask. Next, methanol solution (6.0 mL) of sodium hydroxide (2 wt% of the whole methanol) as catalyst system was added drop wise and then heated up to 45 ℃ with reflux. The reaction mixture was stirred violently for 4 h. After the reaction, the solvent was removed and the products were evaporated using a vacuum oven set at 40 ℃. The yield of modified polymer was 0.365 g, 56%. The Au NPs stabilized by PTMP-PVAc was modified using the same process above.



Scheme S1 Reactivity of the modification of thioether polymer ligands to realize the transfer of Au NPs from organic into aqueous phase.

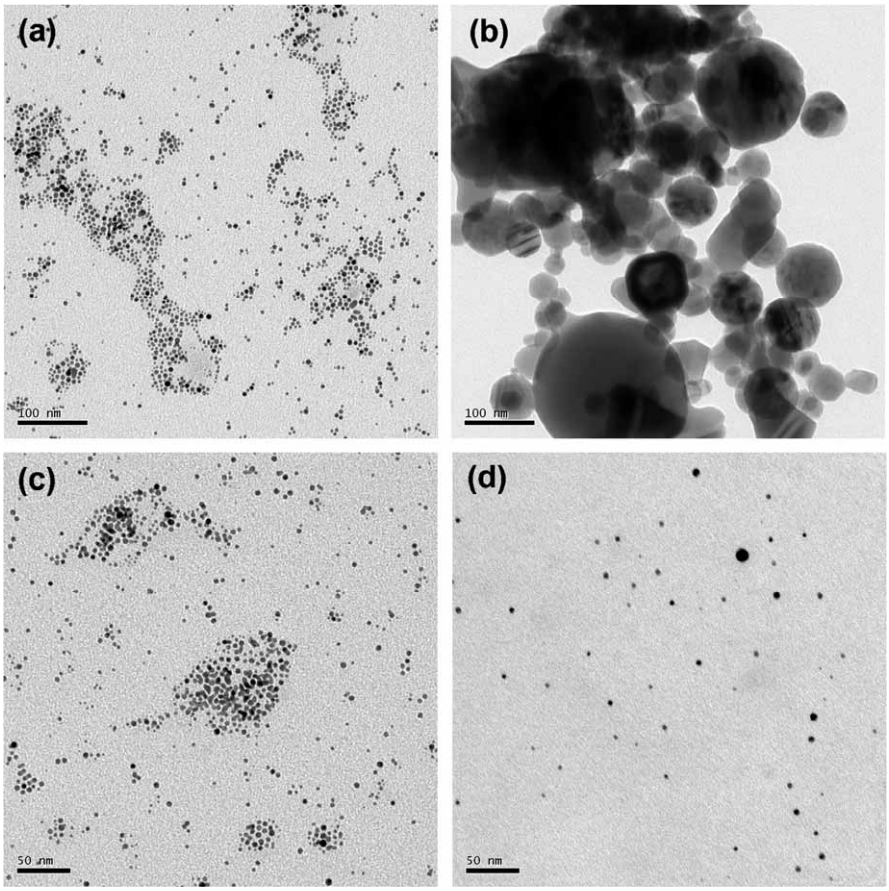


Figure S15 TEM photograph of modification thioether polymer ligands: (a) DDT-PVAc-Au NPs; (b) DDT-PVA-Au NPs; (b) PTMP-PVAc-Au NPs; (d) PTMP-PVA-Au NPs.

S-Ⅳ Ligands exchange

Ligands exchange was introduced to prove the weaker bonding force between the thioeteher polymer ligand (DDT-PVAc) and Au NPs, as compared with thiol ligands dodecanethiol (DDT). 200 μL DDT was dissolved in 15 mL acetone and then added the Au NPs protected by DDT-PVAc (0.050 g). The mixture was stirred for three days at 45 ℃. The mixture was dried by evaporation of solvent in a rotary evaporator and then dialyzed using the centrifugal filter (10000 g/mol cutoff) for another three days. After removed the solvent and dried in the vacuum oven, the sample was dissolved in the toluene.

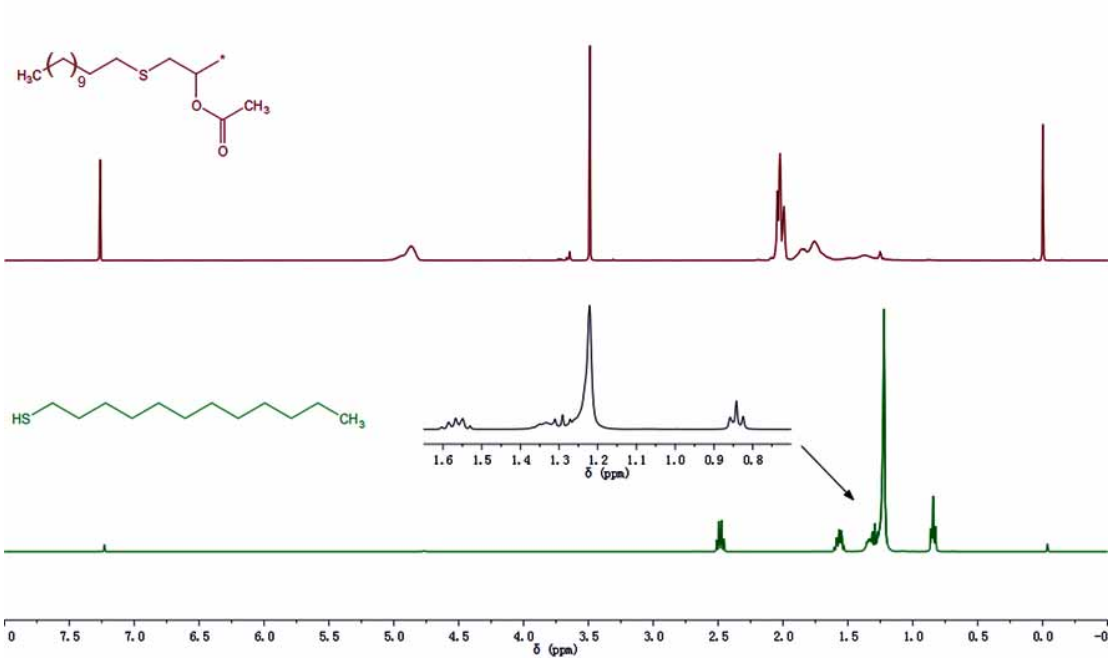


Figure S16 ^{1}H NMR of Au NPs protected by thioether polymer ligand DDT-PAVc (red) and after the ligand exchange by DDT.