Supplementary Material for Chemical Communications

Supplemental Materials for

Construction of Conjugated Molecular Structures on Gold Nanoparticles via the Sonogashira Coupling Reactions

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Materials: All the compounds used in the work are commercial products (from Aldrich or Acros) with the highest quality available unless notified in the following content or in the manuscript.

Synthesis and characterization of 4-iodobenzenethiol: The synthesis of 4-iodobenzenethiol was followed by a reported procedure (see Ref below). To a suspension solution of Zn powder (0.76g, 11.6 mmol) and Me_2SiCl_2 (1.50 ml, 11.6 mmol) in 1,2-dichloroethane (25 ml) was added a solution of 4-iodobenzenesulfonyl chloride (1.00g, 3.3 mmol) and *N*, *N*-dimethylacetamide (1.00 ml, 10.0 mmol) in 1,2-dichloroethane (25 ml). The mixture was stirred at 75 $^{\circ}$C for 2 hs until the Zn was no longer visible. After cooled to room temperature, the 10 % HCl solution was added, and the reaction mixture was stirred for another 0.5 h. The mixture was then poured into water and extracted with CH_2Cl_2, and the combined organic layers were washed with saturated solution of NaCl (30ml × 3) and dried over anhydrous $MgSO_4$. The solvent was removed to give the target compound as a white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.41 (s, 1H) ppm.

Ref: Daniel T. Gryko, Christian Clausen, Kristian M. Roth, Narasaiah Dontha, David F. Bocian, Werner G. Kuhr, and Jonathan S. Lindsey *J. Org. Chem.* 2000, *65,* 7345-7355

Synthesis and purification of Au nanoparticles modified with a mixed monolayer of 4-mercaptophenol and 4-iodobenzenethiol: Preparation of Au nanoparticles (5 nm in diameter, TEM) protected by a mixed monolayer of 4-mercaptophenol and 4-iodobenzenethiol involved two steps. First, Au nanoparticles modified with 4-mercaptophenol were obtained by following the reported procedure (see reference 7). The second step was the place-exchange of 4-mercaptophenol on particle surfaces with 4-iodobenzenethiol. The exchange reaction took one day at room temperature. The purification was achieved through repeated precipitation and centrifugation of crude materials in a mixed solvent of methanol and chloroform. The final product was obtained as deep brown solid. These particles were very soluble in polar organic solvents.

Sonogashira reactions at mAuNP particle surfaces: To a round-bottom flask was added the 500 mg of mAuNPs, a terminal alkyne (excess in molar ratio as compared with available iodo reacting sites on particle surfaces), $Pd(PPh_3)_2Cl_2$ (5% mmol based on iodo reacting sites on particle surfaces), CuI (10 % mmol based on iodo reacting sites on particle surfaces), PPh_3 (20% mmol based on iodo reacting sites on particle surfaces). The flask was evacuated and backfilled with N_2 (3×). The solvent THF (15ml) was added followed by base *i*-Pr_2NH (10 ml). The reaction was stirred at room temperature for 24 h. The solvent was removed under reduce pressure, and residue was then dissolved in CH_2Cl_2, washed with saturated solution of NH_4Cl and saturated solution of NaCl (3×) and dried over anhydrous $MgSO_4$. The solvent was removed and crude product was recrystillation from CH_2Cl_2-Hexane at least three times to give target compound as a deep brown solid.

TEM measurements: The TEM and HRTEM measurements were carried out on a JEOL4000FX. A few drops of Au NPs methanol solution were transferred onto a carbon coated copper grid. The solvent was naturally evaporated at room temperature. The TEM and HRTEM images were obtained at 100 and 200 KeV acceleration voltages respectively. The typical images and size distribution of mAuNPs and **3**-mAuNPs are shown in Figure S1. The histograms of size distribution of 4-meracptophenol-modified Au NPs, the mAuNPs and 3-mAuNPs are shown in Figure S2

Energy Dispersive Spectroscopy (EDS) measurement: Energy dispersive spectroscopy of the sample x-ray fluorescence was carried out using a Link Analytical Systems detector connected to an LPI x-ray pulse processor build in a JEOL 4000 FEX Transmission electron microscope. The collection live time was 300 seconds with a detector dead time of 6%. The spectra of testing the existence of Au and absence of Pd and I elements in **3**-mAuNPs is shown in Figure S3.

^{1}H NMR: ^{1}H NMR spectra (400 MHz) were recorded with a Varian UI400 NMR spectrometer.

Electrochemistry Study: The electrochemistry study was carried out using an Electrochemical Analyzer CH420 (CH Instruments, Austin, TX). The standard three-electrode assembly was employed. A glassy carbon electrode (5mm in diameter) was used as a working electrode. A platinum wire was used as a Counter electrode and the reference electrode was a non-aqueous $Ag/AgNO_3$ electrode. The dry tetrahydrofuran (THF, Sigma Aldrich) was used as the solvent. The supporting electrolyte was tetra *n*-butylammonium hexa fluorophosphate (TBHP, Acros). The volume of solution used for all electrochemical study was 5mL and all the studies were carried out at room temperature. The working electrode was cleaned and polished using alumina powder before and after every trial. The parameters used to generate the excitation function for square wave voltammograms (SWV) were as follows: step size, 4 mV; pulse amplitude, 25 mV; frequency, 15 Hz.

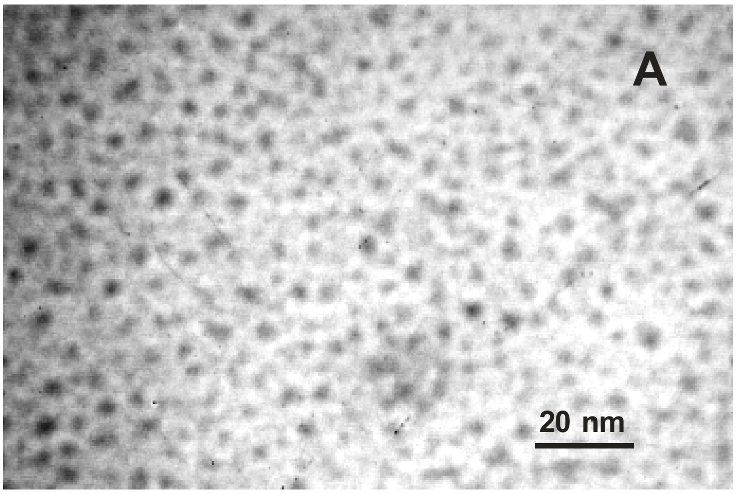
Photon Correlation Spectroscopic (PCS) Experiments. A Coulter N4-Plus instrument was utilized to monitor the stability of surface-modified Au nanoparticles in chloroform at room temperature. The scattered light was detected at 90° from the incident beam. The viscosity and refractive index of the Au nanoparticles solutions were taken as identical to the values of chloroform.

UV-Vis Spectroscopic Measurements. Electronic absorption spectra of **3** and **3**-mAuNPs in chloroform were recorded with a HP8452A diode array spectrophotometer at room temperature.

Fluorescence study. The steady-state fluorescence spectra of **3** and **3**-mAuNPs in chloroform at room temperature were recorded on a Spex Flourolog 1681 fluorophotometer controlled by DM 3000 controller. The excitation wavelength is 325 nm.

Figure S1

A. TEM image of mAuNPs



B. TEM image of **3**-mAuNPs

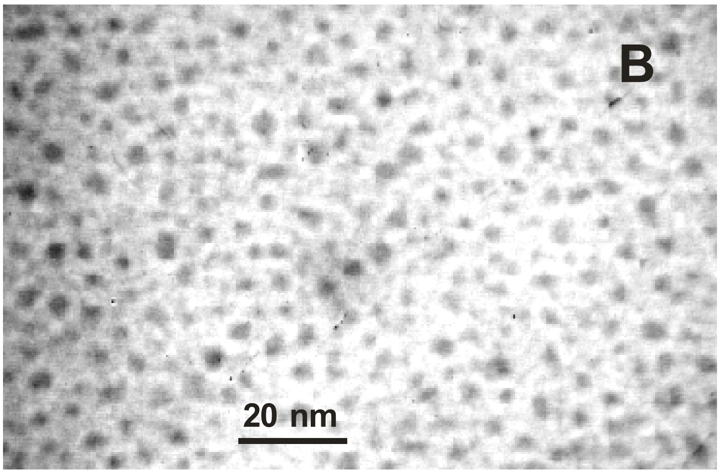


Figure S2

Histograms of Au NPs.

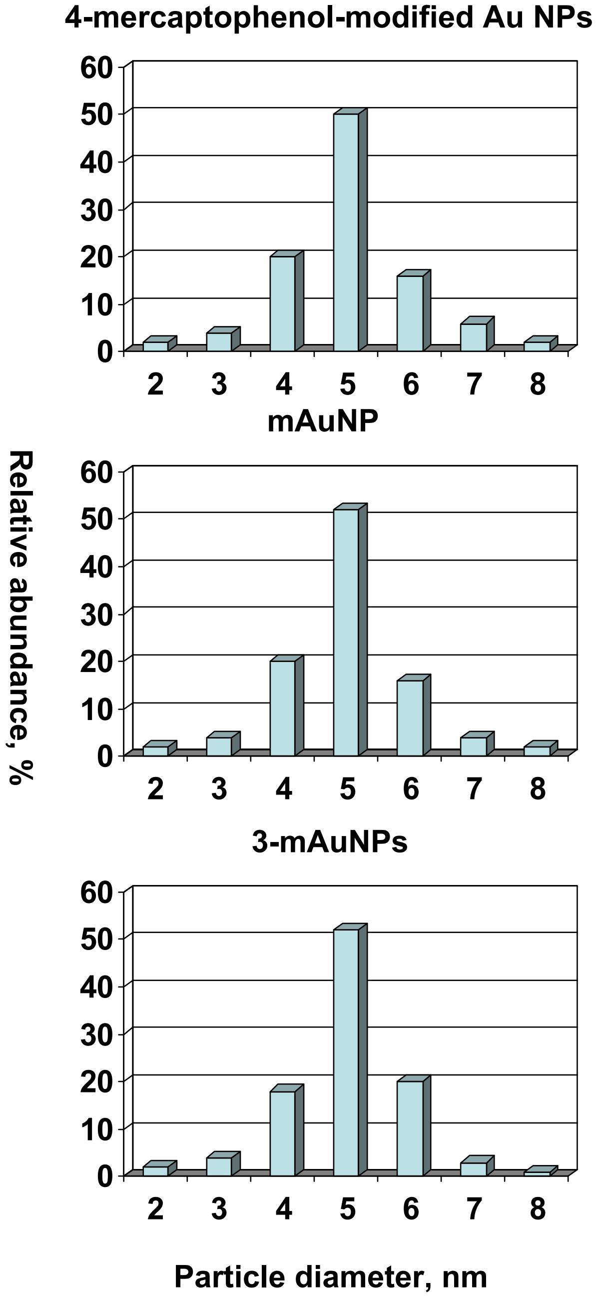


Figure S3

EDS analysis of **3**-mAuNPs