In Situ Observation of Place Exchange Reactions of Gold Nanoparticles. Correlation of Monolayer Structure and Stability

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Supporting Information

Materials:

Thiols used in the place exchange reactions were purchased from Aldrich, and were used as received. (*S*)-2-Methybutyl-4-toluenesulfonate was synthesized according to a reported method.[1] The thiol-Bodipy ligand was synthesized as reported.[2] $HAuCl_4 \cdot xH_2O$ was purchased from Strem. Other chemicals were obtained from either Aldrich or Acros, and were used as received. Dichloromethane (DCM) was distilled over CaH_2 prior to use.

Instrumentation:

Fluorescence spectra of Bodipy release were collected on a Shimadzu RF-5301 PC spectrofluorometer. UV-Vis spectra were recorded on a HP 8452A UV-spectrometer. Proton NMR spectra were recorded using a Brüker DPX-300 spectrometer in $CDCl_3$ solutions at 300 MHz (referenced to residual $CHCl_3$).

Thermogravimetric analysis (TGA) was performed using a TA Instruments, Inc. (New Castle, DE), Model TGA 2950 high-resolution thermogravimetric analyzer. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller. The TGA curves were measured as follows: about 5 mg of each nanoparticle was placed in the TGA pan and heated in a nitrogen atmosphere at a rate of 10°C/min up to 450°C.

Synthesis of (S)-2-methyl-1-butanlthiol

(*S*)-2-methyl-1-butanthioacetate
To a suspended solution of potassium thioacetate (3.4 g, 30 mmol) in dry THF (40 mL) was added (*S*)-2-Methybutyl-4-toluenesulfonate (2.4 g, 10 mmol) at room temperature, subsequently refluxed overnight. Water was added to quench the reaction, and the mixture was extracted with ether. Combined organic layer was washed with water and brine before dried over $MgSO_4$. Concentrated residue was subjected to purification by flash column chromatography and distillation under reduced pressure to yield a colorless liquid (1.0 g, 68%)

(*S*)-2-methyl-1-butanlthiol
To a solution of (*S*)-2-methylbutylthioacetate (1.0 g, 6.8 mmol) in methanol (1 mL) was added oxalyl chloride (0.6 mL) dropwise. After stirring at room temperature over night, the solvent was distilled off at 120 ˚C. Crude product was purified by vacuum distillation

to yield a colorless liquid (0.32 g, 45%). The ^{1}H NMR spectrum of the product was identical to the commercial sample of racemic 2-methyl-1-butanthiol.

Synthesis and characterization of **Au-Fl***:*

Gold nanoparticles covered with 1-pentathiol, AuC5, were synthesized by following a reported procedure.[3] AuC5 (70 mg) and thiol-Bodipy ligand (60 mg) were mixed in 10 mL of dry DCM. The reaction mixture, kept away from light, was stirred under Ar for about 60 hours. The solution was transferred into a 250 mL round bottom flask, and DCM was removed on a rotovap. The resulting black material was washed with hexanes for a few times until no Bodipy fluorescence was seen. The solid was transferred to a 7-mL vial, and further washed with hexanes until no fluorescence was seen under a hand hold UV-lamp. The solid was added 1 mL THF, and the particles were precipitated in hexanes. After centrifugation, the supernatant was discarded. This dissolution-precipitation process was repeated. After drying in vacuum, the solid was characterized by NMR and UV-Vis spectroscopy, and store in a DCM solution in dark.

As expected, the proton NMR spectrum of **Au-Fl** showed broad peak of the corresponding thiol-Bodipy ligand (Figure S1). The lack of sharp peaks in the spectrum indicated the absence of free dye molecules in solution. The UV-Vis spectrum of **Au-Fl** showed strong absorbance of Bodipy dye (Figure S2) as a pronounced peak around 500 nm.

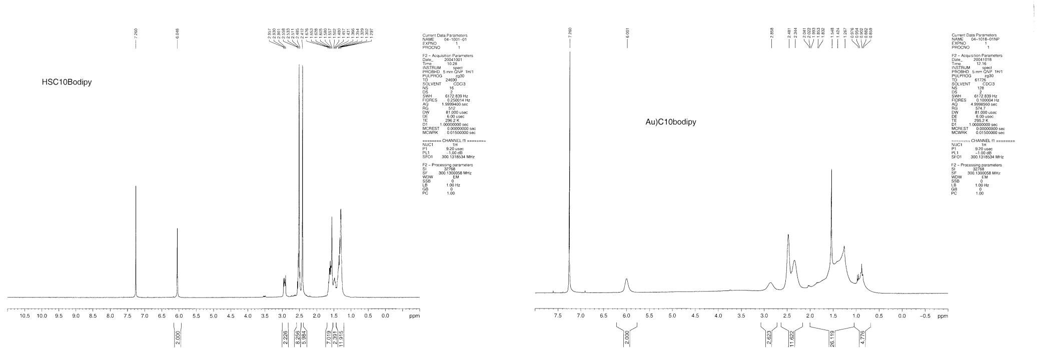

Figure S1. NMR spectra of thiol-Bodipy ligand (left), and **Au-Fl** (right).

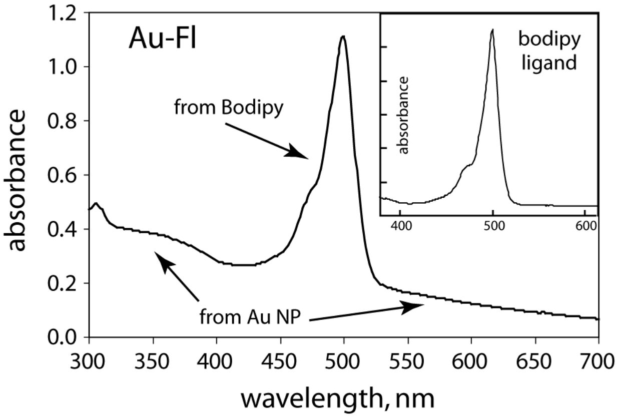

Figure S2. UV-Vis spectrum of **Au-Fl** in a DCM solution. Inset: UV-Vis spectrum of thiol-Bodipy ligand **1** ($\varepsilon = 1.27 \times 10^5$ cm^{-1}·M^{-1}).[2]

Bodipy displacement experiment:

To a 2-mL solution of **Au-Fl** in DCM ($A_{500} = 1.1$) was added a 1 M thiol solution in 1-pentanol (20 μL) to give a final thiol concentration of 10 mM. The cuvette was sealed, and placed in a 23 °C water bath. Fluorescence spectrum of the solution was taken every five minutes for one or two hours. The excitation wavelength was set at 490 nm, with emission spectrum scanned from 500-600 nm. Both of the excitation and emission slits were set at 1.5 nm. For each group of thiols, experiments were carried at the same time for at least twice. The average intensities at 507 nm in the spectra were plotted against the reaction time. Control experiments showed that addition of thiols to thiol-Bodipy ligand solution did not increase Bodipy fluorescence. In addition, no fluorescence increase of **Au-Fl** solution was observed in the time frame of the experiments if thiol was not added.

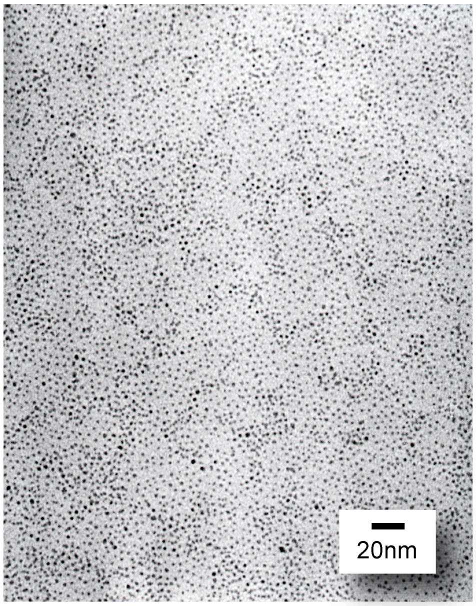

Figure S3. TEM of **Au-Fl** composed of a 2.6±0.5nm diameter Au-core.

Synthesis of C5-thiol covered nanoparticles for TGA experiments:

Thiols used to make nanoparticles were: 1-pentanethiol, 3-methyl-1-butanethiol, 2-methyl-1-butanethiol (racemic), and *S*-2-methyl-1-butanethiol. To an aqueous solution of $HAuCl_4$ (50 mg) was added 30 mL of toluene and 140 mg tetraoctylammonium bromide (TOAB), and stirred for a few minutes. The gold salt was transferred into the organic phase, to which was added 20 μL of thiol. After stirring for a few minutes, a $NaBH_4$ solution in water was added in one portion. The color of the toluene phase changed from yellow to dark brown in less than 5 seconds. The reaction was stirred for another 3 hours before the two phases were separated. The aqueous phase was discarded. The organic phase was added MeOH (~250 mL), and was kept at −20 °C for 48 hours. The particles precipitated from the solution, and were collected by decantation of the supernatant and further centrifugation. The particles were further washed with MeOH (twice) and centrifuged. The particles were dried in a vacuum oven at least overnight prior to the TGA experiments.

Simulation:

Thiol chains were constructed using Maestro modeling software (Maestro 7; Schrodinger Inc.: Portland OR, 2005). Molecular mechanics minimization was performed using MacroModel version 9.0, with energy minimization performed using the AMBER forcefield, with distances constrained between the sulfur atoms at 4.2 Å,

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[2] Shepherd, J. L.; Kell, A.; Chung, E.; Sinclar, C. W.; Workentin, M. S.; Bizzotto, D. *J. Am. Chem. Soc.* **2004**, *126*, 8329-8335.

[3] Boal, A. K.; Rotello, V. M. *J. Am. Chem. Soc.* **2002**, *124*, 5019-5024.